SLOVAK GEOLOGICAL MAGAZINE

VOLUME 9 NO 2 – 3
ISSN 1335-096X

Geological Survey of Slovak Republic, Bratislava
Dionýz Štúr Publishers

2-3/2003

ISSN 1335-096X

SLOVAK GEOLOGICAL MAGAZINE

Periodical journal of Geological Survey of Slovak Republic is a quarterly presenting the results of investigation and researches in a wide range of topics:

- **regional geology and geological maps**
- **lithology and stratigraphy**
- **petrology and mineralogy**
- **paleontology**
- **geochemistry and isotope geology**
- **geophysics and deep structure**
- **geology of deposits and metallogeny**
- **tectonics and structural geology**
- **hydrogeology and geothermal energy**
- **environmental geochemistry**
- **engineering geology and geotechnology**
- **geological factors of the environment**
- **petroarcheology**

The journal is focused on problems of the Alpine-Carpathian region.

Managing Editor: G. Šipošová
Technical Editor: G. Šipošová
Address of the publishers: Geological Survey of Slovak Republic, Mlynská dolina 1, 817 04 Bratislava, Slovakia
Printed at: Alfaprint Martin
Price of single issue: USD12
Annual subsc include the postage

SLOVAK GEOLOGICAL MAGAZINE

VOLUME 9 NO 2 – 3

ISSN 1335-096X

Geological Survey of Slovak Republic, Bratislava
Dionýz Štúr Publishers

2-3/2003

Slovak Geol. Mag., 9, 2 – 3(2003)

Introduction

From 12th to 14th November 2003 the Geoanalytical Laboratories in Spišská Nová Ves organised an international conference „ANALYSIS IN GEOLOGY AND ENVIRONMENT 2003“ on the occasion of 50th anniversary of their establishment.

The programme of the second international conference was focused on the presentation of analytical works in the scope of anorganic and organic analyses of geological and environmental materials, sampling methods and sample decompositions, processing and interpretation of analytical data, monitoring of the environment, quality control and quality assurance of analytical results.

The conference was addressed to the wide range of specialists from analytical laboratories, research institutes and universities.

The Geoanalytical Laboratories in Spišská Nová Ves during their fifty year existence underwent wide range of activities, from classic chemical analytical methods of geological materials as rocks, minerals, ores, solid fuels and all kinds of waters to an application of the most modern analytical methodologies and methods providing analyses of inorganic and organic elements of trace and macro contents. Later the range of the analysed material included also environmental samples as sediments, soils, wastes and vegetal samples. The implementation of a new sequential sample extraction method (soils and sediments) has enabled a new approach to environmental risk assessment of contaminated areas on human health.

The quality of analytical results is guaranteed by an established system of quality control. In 1996 the Geoanalytical Laboratories proved their competence to perform analyses objectively and trustworthily by obtaining an accreditation from SNAS which performed audit according to the requirements of EN 45 000. In 2002 the laboratories were successfully reaccredited according to the European standard EN ISO/IEC 17025.

The papers presented on the conference have been published in this issue of Slovak Geological Magazine. Scientific, language and graphical content of the papers is in full responsibility of the individual authors.

Contents

Slovak Geol. Mag., 9, 2 – 3 (2003), 89 – 91

Fifty Years of Geoanalytical Laboratories in a Service of Geology in Slovakia

DANIELA MACKOVÝCH

Geological Survey of Slovak Republic, Geoanalytical Laboratories,
Markušovská cesta 1, 052 40 Spišská Nová Ves

The basis for the mineral exploration and technological treatment and evaluation are good analytical results. The history of geoanalyses in Spišská Nová Ves began on 1st December 1953. The Laboratory was established as a part of Geological Survey n. c. Its main aim was to perform the analyses of Fe, Mn and magnezites. At the beginning only classical analytical methods were used for the determinations. Later new and modern instrumental methods like Optical Emission Spectrometry (OES) and Polarography were introduced. At that time the Controlling and Application Department was established in the laboratory. The main goal was the application of new analytical methods as for example silicate analyses including trace elements analyses.

The capacity and the extent of laboratory works were growing until the first half of sixty years. At that time the laboratory had an important role among all other laboratories in Czechoslovakia. A great development of analytical works, which were focused on the analyses of trace elements, took place. Docimastic method for the determination of Au and Ag and Atomic Absorption Spectrometry – one of the most progressive analytical method of raw materials were introduced. The later mentioned method was applied as the first in the resort of geology in Czechoslovakia. The other methodologies as for example sinter and pressure sample decomposition and ionselective electrodes for the determination of F and Cl were established. Semiquantitive methods OES were extended of quantitative determination of Sn, Mo and W. The analyses of all types of water started in 1965.

The cooperation with the laboratories of Central Geological Institute (ÚÚG), Geological Survey in Prague and in Brno and the Institute of Raw Materials (ÚNS) in Kutná Hora was very important for the developing and validation of analytical methods for various types of geological materials – silicate rocks, limestone, magnezite, dolomite, glass sand, ceramic raw materials, Au-Ag ores, polymetallic ores, Cu-Pb-Zn ores and Hg ores. Together with the development of methodologies, in house reference materials for analytical quality control were also prepared. The laboratories of ÚNS in Kutná Hora, ÚÚG in Prague, Geological Survey in Spišská Nová Ves participated in analytical works.

The development of geological research at the end of 70th until the first half of 80th required the extending of laboratory works according to the amount and development of new analytical methods. A new and modern instrumental technique – Atomic Emission Spectrometry with Inductively Coupled Plasma (AES-ICP) – ARL 33 000 was bought in 1976. It was the first analyser of this kind in the resort of geology in Czechoslovakia. This technique replaced classical analytical methods and it widened the range of determined trace elements with a low limit of detection. The modernization of instrumental park continued in the following years. Elementary analyser Carlo – Erba for the determination of elementary C, H and N in coal and organic materials as well as Atomic Absorption Spectrometer AAS-875 Varian were added into the laboratory facilities. Simultaneously AES-ICP-ARL 34 000 for the analysis of silicate and trace elements – Cu, Pb, Zn, Ni, Co and Cd and X-Ray diffractometer DRON were bought in 1981. Next year Adiabatic Calorimeters IKA C-400 for the determination of gross calorific value, Gas Chromatograph – CHROM-4a and Derivatograph – Q 1500 D were purchased too.

In the second half of 80th the laboratory reached its largest qualitative and quantitative improvement. The range of analytical and special geological works covered all needs for geological, hydro-geological, geological engineering and geochemical works. Due to the high level of laboratory works and new analytical instruments the laboratory was included among the best laboratories not only in Czechoslovakia but also in the countries of Council of Mutual Economic Assistance (Comecon). All the following analyses were performed in the laboratory:

- analyses of Fe – ores,
- analyses of coloured metals ores,
- analyses of glass sand for special purposes,
- analyses of white salt,
- analyses of silicate and carbonate rocks,
- analyses of soils,
- analyses of surface and underground water,
- determination of Ag, Al, As, Au, B, Ba, Be, Bi, Ca, C, Cd, Ce, Cl, Co, Cr, Cs, Cu, Eu, F, Fe, Ga, Ge, H, Hg, In, K, La, Li, Mg, Mn, Mo, N, Na, Nb, Ni, P, Pb, Pr, Rb, Sb, Sc, Se,Si, Sm, Sn, Sr, Ta, Te, Ti, V, W,Y,Zn, Zr,
- qualitative spectral analyses
- semiqualitative spectral analyses in SPD scale,
- determination of free SiO_2 and analysis of mining air – CO_2, O_2, CH_4, Ar, H_2, H_2S, He, N_2, Ne,
- geotechnical tests of soils,

Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava 2003 ISSN 1335-096X

- technological tests of brick raw materials, clay, kaoline, bentonite for ceramic purposes,
- technological tests of stone, sand, gravel for building, founding and glasswork purposes,
- technical tests of solid fuels including the determinations of C, H and N,
- technological tests of non-metallic materials,
- chemical analyses of atypical samples,

Gradually other modern equipment was introduced into the laboratory:

- Wavelength-dispersive X-ray fluorescence spectrometer PHILIPS PW 1404 for the analysis of geological materials with non-destructive technique from pressed pellets and glass bead,
- a new model of Atomic absorption spectrometer Varian AA - 40 with electrotermal atomization - GTA 95 and hydride generator - VGA - 76 in 1986,
- Isotachophoretical analyser for the determination of anions in water in 1987,
- TMA analyzer for the determination of Hg, X-Ray diffractometer - URD-6 in 1989.

Special geological, mineralogical, petrographical and geochemical works were performed in the laboratory. These works were oriented on genezis of material, setting up of the basis for prognosis of raw materials perspectives and for the study of their structure and technological properties. Laboratory works were focused on the identification of minerals using X-Ray diffractometry and DTA, optical spectrometry and Rtg microanalyses, preparation of mineralogical polished specimen with automatic technique Logitech.

In 1991 the laboratory was again modernized. Sequential AES-ICP spectrometer Liberty 200 with ultrasonic nebuliser and Atomic absorption spectrometer Varian AA-20 for the determination of major and trace elements with low limits of detection and Gas chromatographs GC 3400 with Flame Ionization Detector and Electron Capture Detector for the determination of organic pollutants were added.

In 1992 the range of analysing organic compounds was extended of polycyclic aromatic hydrocarbons and the identification of unknown organic compounds with gas chromatograph Saturn II with Mass Detector. The laboratory was equipped with the most modern technology for the isolation of organic compounds from soils and stream sediments with Supercritical Fluid Extraction and the technique of Purge and Trap with concentrator Tekmar for the isolation of volatile halogen hydrocarbons and volatile aromatic hydrocarbons.

Infrared spectrometer Mattson for the determination of drinking and other types of water pollution as well as for the determination of soil pollution by oil contamination was bought in 1983. AMA automatic analyser for the determination of Hg in water and solid materials with a very low limit of detection was introduced too.

The department of sample preparation was very good equipped with jaw crushers, mills, vibratory ring pulveriser, pulveriser with crinding barrels from agate, automatic rotary divider all made in Retsch and Fritsch company.

The largest extend of laboratory works was achieved in 1991. After then the decrease and permanent reduction of state investment in the area of geological and research works caused the change of analytical works from the analysis of geological materials to the analysis of environmental samples.

In 1994 the laboratory started to prepare for the accreditation according to the requirement of EN 45001. After the fulfilling of accreditation criteria set by the European Technical Norm EN 45001 in 1996 the Geoanalytical Laboratories became accredited by the Slovak National Accreditation Service.

Since 1996 The Geoanalytical Laboratories are a part of Geological Survey of Slovak Republic (GSSR). The GSSR was established by the Decree of Minister of the Environment as a contributory organisation of the Ministry of the Environment. The GSSR´s headquarters are in Bratislava, but its activities cover the whole Slovakia.

Geoanalytical Laboratories of GSSR were established by the Decree of Minister of Environment on 25th March 1997 as a Reference Laboratory of the Ministry of Environment of SR (RL) for geology and analysis of geological materials and rock environment. The activities of RL are aiming mainly at:

- reliability of analysis and test results for state administration,
- monitoring and control measuring,
- continual improving and holding high level of quality of environmental measuring,
- harmonise conditions for input of Slovakia into market of EU.

Since 1996 the Geoanalytical Laboratories as a RL were an active partner in the project of bilateral cooperation between the Ministry of Environment of SR and Danish Environmental Agency entitled *Implementation of Laboratory Structure to Provide Adequate Analyses for the Environmental Management of the SR.*

The GAL co-operated internationally with laboratories of geological surveys of Europe in testing and developing analytical methods in geochemical and environmental monitoring, in sample collection techniques and in putting up systems to support and to control quality of analytical data. GAL provided homogenisation services for *Global Geochemical Baselines Project and for the European Geochemical Atlas.*

The most significant event in the year 2002 was the re-accreditation of the laboratory according to the European Technical Norm EN ISO/IEC 17025. Geoanalytical Laboratories successfully finished the re-accreditation process and received certificate on accreditation for analyses of geological materials, minerals, ores and non-metallic raw materials, solid fuels and products of combustion, soils, sediments, plant materials, food, waste, determination of physico-chemical, hydrobiological, microbiological and ecotoxicological indicators in waters and taking off samples of coal, soils and sediments.

In 2003 the laboratory was again modernized. Sequential AES-ICP spectrometer VISTA –MPX with CCD was bought, which allows to determine trace elements with a very low limits of detection.

Geoanalytical Laboratories as a Reference Laboratory of the Ministry of Environment organise the inter-laboratory proficiency tests for Slovak laboratories. This programme is a part of Quality Control Programme of the Ministry of Environment for Slovak environmental laboratories. Proficiency test is an external control of analytical system, performance of laboratories, and enable the participants to detect unsuspected source of errors and subsequently made remedial actions.

The Laboratories regularly take part in international interlaboratory tests and certification programmes for geological and environmental samples. These programmes are useful source of reference samples which can be put to good use internally. In the last four years Geoanalytical Laboratories prepared through interlaboratory exchange programmes two certified reference materials of chemical composition Zeolite1 and Bentonite1. The both reference materials were certified by the Slovak Metrological Institute.

The Geoanalytical Laboratories of Geological Survey of Slovak Republic have 50 – year experience in the performing of the rock and metallic ore analyses. Nowadays they provide comprehensive laboratory analytical service for geological, geochemical, hydrogeological exploration and research, environmental monitoring according to the requirements of the Ministry of Environment and other state and private organisations.

Slovak Geol. Mag., 9, 2 – 3(2003),93 – 98

Development, Present State and Possibilities of Chemical Analyses in Study of the Earth

EDUARD PLŠKO

Donská 97, 84106 Bratislava, Slovak Republic

> Nec tantum segetes alimentaque debita dives
> poscebatur humus, sed itum est in viscera terrae
> quasque recondiderat Stygiisque admoverat umbris,
> effodiuntur opes, irritimanta malorum.
> *Publius Ovidius Naso (43 – 18),*
> *Netamorphoseon libri* ***103****, 49 –52.*
> Concerning the soil, it was not more expected only
> crop and ensuring of rich food claims, but it was gone
> in the Earth bowels and wealth representing temptations
> of evil which had been hidden placed in the shades of
> the subterranean river Styx, were unearthed.
> free translation by E. P.

Abstract. The lecture presents first primitive attempts of chemical characterisation. The very beginning of chemical analyses is connected mainly with mining collected with the need of geological prospection. First analyses of main components in ores were performed preferably by dry way. The necessity to quantificate present components inclusive trace elements lead to elaboration of more effective wet procedures. Because of laborious and time consuming dissolution connected with danger of possible contamination, solid sampling procedures gain their revitalisation.

Main persons who contributed to the development and application of different new progressive analytical procedures in our country are remembered and their contribution presented.

Some problems in the communication between geologist and analytical chemists are discussed and not sufficient citation of analytical publications giving necessary information on the metrological parameters of the used analytical procedures describing the reliability of the gained results and consequently of geological conclusions obtained by their use is criticised.

Recent essential decay of mining and consequently also of geological works supplying well equipped analytical laboratories with samples bringing necessary funds for their existence and growth caused that it had been necessary to seek new orientation which has been found in the focusing of the original geological laboratories on solving of environmental problems where apart from the original orientation the organic analyses and speciation play a considerable role, but only so further job for these laboratories performing now extremely important tasks for the sanation and revitalisation of our polluted environment could be ensured and so its preservation for future generations achieved.

Key words: history of chemical analysis, geological analysis, environmental analysis, citation problems, analytical procedures, Slovak analysts.

Introduction

The development of intelligent beings represented by *homo sapiens* has led to the situation that already its ancient predecessors had started, namely with the use and later also with the production of their first primitive tools, to take notice of their surroundings and after the first recognising phases they began to categorize different objects according to their characteristic properties and to divide them in greater groups having common generalised features. First primitive origin of chemical characterisation of different materials can be found long ago at the distinction whether a given stone is by its hardness, cleaving ability and workability fit for the production of different tools, as primitive knives, axes, arrow points etc. or if it can be used by mutual rubbing for the preparation of necessary fire, or it can serve by thermal treating as raw material either for glass, or some at that time known very useful metals serving for decorative purposes, for everyday aims and mainly for the production of more perfect weapons, if a given clay is suitable for the production of ceramics for everyday, cult or decorative use.

As a matter of fact the cited and similar knowledge represents the cradle of analytical chemistry which very formation was determined first after some thousand years later by origin and later development of different handicrafts and by the perfection of mining and metallurgy and last but not least by introduction and bloom of alchemy which, it is true, has found neither the *philosopher's stone* enabling the gold preparation, nor the *elixir vitae* ensuring everlasting life, but it discovered a multitude of precious knowledge on chemical properties of different materials.

Origin of chemical analysis

One of the most important milestones in the cultural development is represented by the transition from the stone age to the production and use of metals. In the nature one can find only very restricted number of metals in native elemental form (in particular gold and silver). The production of the majority of metals was so conditioned by the finding and mining of appropriate ore and elaboration of a convenient, mostly complicated thermal metallurgical technology. The described situation, if one wanted to rich the corresponding aim required an as good as possible characterisation of all used objects and technological steps. According to that the first attempts of a more serious chemical characterisation can be sought in connection with metal production.

As it is written in some further lines of the Ovidius' poem presented as the preamble, there was discovered iron and even more useful gold, and wars fighting with the both named metals started and the mentioned temptation of evil has been realised. How excellent prophecy (!) in which, unfortunately a significant role was played ,if one wants or not, also by analytical chemists beginning their „handcraft" even in search of ore deposits (analytical chemistry enabling and significantly supporting geological survey) and their following treatment inseparably connected with wastes (chemical analysis of environmental pollution). Our conference is devoted to both named applications of analysis; in the first half aimed by elucidation and exploitation of positive gifts devoted by our Earth and in the second half by elucidation and possible reduction of negative influences of the first named activities on our Earth. I therefore dared in the title of my contribution to unify the both approaches of the conference in common study of the Earth which contains, as positive, as negative influences in question.

First primitive tools for chemical analysis

As the first aimed object of, one can say, chemical study of the Earth was beyond doubt in search for row materials usable in metal production, i. e. for ore deposits. In order to distinguish between ore and gangue (vaste rock) the characterization of ores was performed originally by their visual (colour, shine, crystalline appearance etc.) and some physical properties (great weight, breakability, hardness etc.). This simple approach was, however, in many cases unsufficient, if one needed to determinate the kind of metal obtained after the metallurgical treating (lead, cadmium, antimony, zinc, tin, copper, iron?). For to solve the mentioned problem rapid and simple analytical procedures by dry way were worked out consisting according the literature (Treadwell, 1918) in the investigation of fusibility, colouring of colourless flame (fore – runner of spectral analysis), volatility, behaviour at reduction and oxidation, colour of sample-borax mixture pearls prepared on platinum wire eye in oxidizing and/or reductive city gas flame, (Minczewski et al., 1975).

The greatest role was, however, played by classical old special thermal treating of the investigated sample mixed with twofold amount of waterless soda put in a small pit made on plane charcoal surface and heated by candle flame oriented using blow pipe on the sample mixture. The properties of small formed metallic ball (so called regulus) or the colour of a deposit around the thermally treated area indicated the presence of different elements. The last, relatively powerful method survived during very long time, since middle ages, practically till the middle of the last century. Practically myself I had yet an exercise in the mentioned procedure in the university practicum of mineralogy. The method enabled identification of a lot of elements: Au, Ag, Cu, Pb, Sn, Sb, Zn, Cd, Co, Mn, Fe, Pt, As (Ormándy, 1904). To a similar kind of analytical procedures belongs also the so called cupellation enabling even quantitative determination of precious metals. Nowadays these methods have not been more described practically in any textbook on analytical chemistry and consequently almost forgotten. As it is clear from the explained exempla, the first attempts to perform a chemical characterisation of materials have been in a close alliance with the metallurgy. A more comprehensive review of the development of metallurgical analyses is described in a separate work (Plško, 2000) where the crucial contributions achieved by Albertus Magnus (1193–1280) and Georg Bauer known as Agricola (1494-1555) are discussed. I mention the classical simple analytical procedures only because of the recent revival of recent dry way methods known as solid sampling which will be dealt with in the chapter devoted to expected trends of chemical analysis for the study of the Earth.

The birth and growth of quantification

Successively growing demand for quantification, which could not be fulfilled with exception of cupellation by the, in their principle qualitative, introduced simple procedures led to the development of mainly wet methods ensuring the claimed reliability (precision and accuracy) but for the price of the necessary, slow and expensive transfer of the, in the greatest deal solid samples into solution, connected even with the contamination danger caused by the used chemicals, especially in the case of trace analysis.

The quantification needs in mining and metallurgy led also to the description of content in the terms of concentration describing practically how much metal can be obtained from a given mass of the ore in question. This, otherwise, practical expression which has been used till now has, however, no thermodynamic sense, it does not correspond to any thermodynamical state unit and apart from that is restricted by zero in the lower, and by e. g. 100% in the upper range. That is because it is not available for any serious statistical evaluation for the description of content or amount of the analyte (Plško, 1998).

Extraordinary richess of metal ore deposits in the Slovak area (Au, Ag, Cu, Fe etc.) and their exploitation even since some millenia caused also an internationally significant high level of the corresponding analytical characterisation and quantification which is reflected also in the foundation of the first technical University for mining of the World, the *Mining Academy* in Banská Štiavnica (Schemnitz) in 1762 where chemistry belonged to basic studied topics.

In difference to the development of various analytical methods enabling the determination of metal content in corresponding ores and products of their technological treatment which can be followed since ancient ages, analytical information on the composition of waste and other rocks having practically nothing to do with metallurgy, as well as the analysis of water, even gas samples are of expressive later time beginning first only with the scientific formation of analytical chemistry conditioned in eighteenth century by the refuting of the flogiston ideas by the french scientist Antoine Laurent de Lavoisier (1743 and decapitated 1794) and realised, as generally accepted, by the work of the swedish chemist Jöns Jacob Berzelius (1779 – 1848).

Quantitative analytical procedures of the so called wet way began with gravimetric procedures used mainly for the determination of main components as SiO_2, CaO, MgO, Fe_2O_3,. Al_2O_3 , etc. Among them the gravimetric determination of SiO_2 has, as one of the most reliable, survived practically till now and is eventually replaced only by the X - ray fluorescence results. Volumetric methods completed in the middle of the last century by complexometric titrations and colorimetry developed in the UV-VIS spectrophotometry and some separating and electroanalytical methods inclusive the for Czechoslovakia representative polarography have closed so the so called classical sphere of analytical methods used for the study of Earth. Not satisfactory detection power and rather poor selectivity of these methods required the application of more powerful procedures.

Among the more recent analytical methods used for the study of Earth, metrological, as well as economical parameters of which had better fulfilled the demanded parameters, an extraordinary role has been played by X – ray fluorescence, electron microprobe, optical emission spectroscopy with arc and later with laser or ICP excitation, equipped also with mass detection, atomic absorption spectrometry with flame, or electrothermal atomization, chromatographic, especially in our country comprehensively studied and improved isotachophoresis and in the last time it is possible to follow also a revival of progressive electrochemical methods represented mainly by new approaches based on coulombmetric principle when one mentions only the mostly applied.

In accordance with the title of my lecture I originally intended to devote its content to the valuation the possibilities of the enumerated methods but when I obtained the 2nd circular with the program of the conference, I saw that there would be presented about 15 contributions with this orientation. It is certainly not my attempt to take the wind from the sails of other contributors and to repeat information which could be better presented by selected our best specialists in the field in question, I decided therefore to focus my lecture preferably on task of analytical characterisation in geological sciences with special orientation on survey of usable row materials and on persons who played in our country a significant role in the development and application of methods for the study of Earth, as well as on some problems of communication between geologists and analytical chemists and of evaluation and presentation of analytical data.

The role and tasks of chemical analysis in geology

In spite of the meaning, unfortunately of some yet living geologists, their original exclusive tools i.e. the hammer and compass have become with the scientific progress not more satisfactory for to solve adequately the pretentious problems of recent tasks on the study of Earth and so a comprehensive laboratory treatment (mineralogical, petrographical, structural and last but not least chemical characterisation) of the investigated samples represents a requirement without which any serious conclusions can be achieved.

The task of analytical chemical results for a successful geological survey can be in principle summarised (Ostroumov, 1979) in the following items:

1. Determination of concentrations for main and accompanying useful and interfering elements in the investigated ore, as well as for element contents in the surrounding waste rocks for to preliminary determinations of the ore deposit contours.
2. Determination of elemental composition for to determinate genetic and economic evaluation of the investigated economically perspective area.
3. To ascertain elements serving as indicators of ore mineralization.
4. Systematic geochemical study of large areas without any primary economical aim; basis for the formation of geochemical maps.
5. Gathering data for the solution of general genetic questions.
6. Evaluation for some geological engineering tasks (construction of big buildings, roads, tunnels, barrages etc.)
7. Water analyses, (drinking, mineral, mine water etc.) for finding new sources, evaluation of corrosion, or precious geochemical information.

The presented list has no pretension to completeness but it clearly shows the significant necessity of analytical data for the development and even existence of modern geological science which significant role has unfortunately very often had not the corresponding acknowledgement and sometimes has been even practically neglected and put in a position of simple servant although it is generally clear that without a reliable knowledge of chemical composition of geological objects no progress would have been possible.

Analytical chemists therefore studied the corresponding literature and on the basis of their experiences and knowledge worked out sometimes considerably complicated exacting procedures in order to fulfil, as well as possible, the demanded parameters, validated their reliability using different analytical methods or expensive certified reference materials obtaining of which was owing to the known lack of corresponding funds sometimes extremely complicated and in the majority of cases was all the gained necessary information published. Analytical methods of the described high quality were then applied on hundreds of delivered samples sometimes, alas, even without the necessary characterisation or several times representing useless redundance coming from the same locality taken by different or even by the same person. The results were used by geologists for publication in which plenty of citations on possible and impossible geological works was presented but almost in all cases without any citation of the corresponding publication describing the used analytical method where one could find a complete information on the reliability of the gained results without which the presented geological conclusions have not been trustworthy at all. In some publications is at most presented the name of the analyst, (e. g. Hovorka,1972) what belongs more in the sphere of ethics but does not give any metrological information necessary for the acceptance of the presented results. There exists in fact only very restricted number mainly of older geological works where the analysts are included as co-authors. On the other hand, as a deterrent example of Slovak geological citation customs I dare to notify that there exist basic works, e. g. a monograph on ultramafites, (Hovorka,1978), where a detailed description of the applied analytical procedure worked out by other authors and later also published with the necessary checking of its metrological parameters (Medveď et al., 1979) is presented practically as own with great amount of results without any indication where and by whom they had been obtained and this in spite of the fact that a description of a method for spectrochemical determination of microelements in silicate rocks containing also a comprehensive study of reliability of obtained results f has already been published long ago (Medveď et al., 1974).

I am pleased to hear that in the last time this situation had been eventually changed and in several cases analytical chemists have been incorporated in research group and consequently in the list of authors of the corresponding publication. One can only hope that this practice will improve also the citation of analytical chemical publications in geological works and so help to the acceptability of their conclusions.

Evolution of chemical analyses of geological materials in our country

The necessity of characterisation and quantification for the geological survey of economically interesting ore deposits forming supposition for mining enterprises, ore-dressing plants and consequently metallurgical plants forced to establish local analytical laboratories enable to perform simple necessary determinations. I personally remember such laboratories e. g. at the copper mine in Slovinky having worked yet in the middle of the last century and of course in Rudňany. Systematic, more general analytical development and application was, however concentrated in state geological enterprises, Universities and later also in the Geological Institute of the Slovak Academy of Sciences.

Originally, the so called classical methods based on gravimetric and volumetric determinations of main components in minerals and rocks were performed. As important specialists in this field can be mentioned at least Doc. RNDr. Ján Jarkovský, DrSc. from the State Geological Institute in Bratislava, Ing. Jozefa Polakovičová, PhD. from the Geological Institute of the Comenius University in Bratislava and Jozef Ambruš from the Geological survey in Spišská Nová Ves. The gained information was gradually completed also by some data on the trace content of some elements using colorimetric and later also polarographic methods performed by Ing. Vladimír Streško, PhD. from the Geological Institute of Comenius University in Bratislava and Ing. Pavol Leštak in the State Geological Institute in Bratislava.. A great progressive break in the determination of trace elements was set in by the introduction of optical emission spectroscopy. First spectrochemical determinations of trace elements in geological samples were performed in the middle of the last century in the State Geological Institute in Bratislava by RNDr. Gejza Kupčo, PhD. who can be so in our country named as father of this, later extremely important and wide-spread effective analytical method. Another pioneer of spectrochemical analysis in Slovakia, Prof. Ing. Mikuláš Matherny, DrSc. (who worked in the group of member of the Slovak Academy of Sciences Dimitrij Andrusov in the Comenius University, perhaps the first among our leading geologists having recognized the role of analytical chemistry in the study of the Earth) has to be prized also as an indefatigable propagandist and organiser of numerous seminars, symposia and conferences with spectroscopic themes. In this connection I dare to mention also my modest contribution in having worked out a system of methods for quantitative spectrochemical analysis of trace elements in sulphide minerals, silicate, carbonate, weathered rocks, soils and water, supported by the validation on the basis of analyses performed with other independent procedures or if available on certified reference materials, beside several more general, theoretical contributions to the own technique (scatter diagrams, distribution of results, handling results below limit of detection etc.).

At the begin of seventies a new powerful analytical method represented by atomic absorption spectroscopy was introduced also in our country in the common laboratories of the Slovak Academy of Science and Comenius University by Ing. Eduard Martiny, PhD. and Ing. Vladimír Streško, PhD. In this connection I would like to remember the unselfish aid of the world known expert RNDr. Ivan Rubeška, CSc. from the Geological Institute in Prague who helped to a fast and large application of this effective method. Atomic absorption spectroscopy was then employed also in the Dionyz Štúr Geological Institute (recent name of the State Geological Institute) in Bratislava by Ing. Mária Klinčeková, as well as in the Geological Survey in Spišská Nová Ves by Ing. Eliáš Feriancík, PhD.

Some years later the first spectrometer with excitation by inductively coupled plasma enabling multielemental analysis with good detection power and reliability for a wide range of analysed geological materials was set in use in the Geological survey in Spišská Nová Ves by Ing. Ľuboslav Blahut, PhD. and in the Geological Institute of Comenius University in Bratislava, introduced and operated by myself and RNDr. Jana Kubová, PhD who belongs to the best experts of this method in our country. In the last years we lived to see also the first mass spectrometer with inductively coupled plasma ion source in the Research Institute for Water in Bratislava operated by Ing. Adriana Shearman, PhD. and representing one of the most effective tools for the determination of trace elements. At this occasion I consider as suitable to remember also, at least some, czech colleagues as RNDr. Zdenek Šulcek, CSc., from the Central Geological Institute in Prague, RNDR. Jaromír Litomiský, CSc. and Ing. Josef Dempir, CSc. from the Institute of Mineral Raw Materials in Kutná Hora, RNDr. Jiří Toman, from Geological Survey in Brno. With these colleagues and others even from different not only European countries we were in very close fruitful contacts and cooperation and also in good friendship for which I would like to express them our sincere thanks.

Apart from analytical procedures based on spectroscopic principles enabling mainly the determination of cations of elements with metallic character, isotachophoresis which was in our country investigated and perfected by Prof. Ing. Samuel Stankoviansky, further developed by Prof. RNDr. Dušan Kaniansky, DrSc. from the Comenius University in Bratislava and brought until the commercial production of corresponding Slovak instrumentation. This method enables also the determination of anions with a detection power needed by recent requirements. Last but not least, in our country was developed by Doc. Ing. Ernest Beinrohr, PhD. from the Technical University in Bratislava. an electrochemical procedure based on coulombmetric principles enabling the determination of numerous cations and anions in a large concentration range. The corresponding instrumentation equipped with the necessary automation and robotization is industrially produced in Slovakia and commercially available too.

Past and contemporary objects of investigation, possible trends for future

As it follows from the presented information, analytical work oriented on the study of the Earth was in the past oriented mainly on geological materials.

According to the model with enormous extent of geological service which existed in the Soviet Union where immense huge geologically not yet surveyed territories had to be recognised and utilised for mining of different interesting raw materials, in socialist Czechoslovakia where mining has existed since several millennia and geological survey of the relative small area performed since some centuries possessed plenty of information, similar too large geological service was established.

This situation concerned analytical chemical laboratories too and it was necessary to find corresponding occupation for their staff. As known, all activities were in that time organised and commanded by political bodies, represented in this case by the Geological bureau having the position of a ministry but obeying all fictions of the Council of mutual economical help (better known as COMECON). According to that, we survived besides our productive collaboration with geological colleagues different analytical campaigns. I shall try to list at least some most significant ones:

„Unified analytical methods“ obligatory for all laboratories of the Czechoslovak geological service which project should ensure the comparability of results gained in different laboratories. A great shortage of the project was that it restricted any research leading to new progressive, more effective analytical procedures codified for longer time the present, not always the best state of art. This project should have been widened for the whole COMECON and we were forced to apply different soviet procedures like the blowing of powdered samples in arc discharge. Fortunately it was not enough time for its realisation. The only advantage of the project was the creation of an extensive set in that time practically inaccessible certified reference materials which were however analyzed in several different laboratories but in the fact with the same obligatory analytical methods so that the randomization of possible systematic errors of the prescribed method was impossible and consequently the accuracy of certified values could be lower.

Another analytical campaigns including practically all our geological laboratories was the determination of rare earth elements which should have been gained from Vietnamese ores and determination of gold which suddenly became interesting in connection with the occurrence in Middle Bohemia, if to list only the most important.

Political changes in 1989 in our society followed by great economical transformations caused also a deep upheaval in geological sphere. The majority of our mines has been closed, geological survey became eventually unnecessary and the extensive system of well equipped expensive analytical laboratories remained practically without any future use in the original state. It was therefore necessary to decide between their liquidation or to seek new analytical programs which could maintain their further existence. Growing interest of the new society and strong pressure on our state management concerning a wide monitoring and following improvement, or better said rescue of our considerably polluted environment by insensitive activities of the previous mining and industry granted a grateful possibility to continue with analytical activities in a similar direction, perhaps after some extension on more organic materials by analyzing solid, liquid and gaseous samples as soils, dumps, waste waters and gases. For this new purpose practically total equipment used for geological analyses, as well as of skill and experiences of the analytical staff having worked with geological samples can be well applied.

What concerns future trends in the environmental chemical analysis one can observe eventual leaving wet procedures requiring complicated, expensive, slow and environment loading dissolving of samples and return to direct analysis of solid materials using so called solid sampling e. g. in electrothermal evaporation or atomization with following application of atomic absorption, or optical emission spectroscopy with inductively coupled plasma. For to solve many environmental problems is in many cases a simple elemental analysis not satisfactory and different appropriate speciation procedures have to be elaborated and applied too.

As conclusion it is possible to state that the chemical analysis has his significant role by fulfilling pretentious gaining of information also in the changed conditions oriented on a better knowledge and improvement of our ill environment, this position will be retained and I hope that also highly prized till many coming years what is my cordial wish.

References

Hovorka, D. (1972): Katalóg chemických analýz, Náuka o Zemi, VI, Vyd. SAV Bratislava, 1-220.

Hovorka, D. (1978): Geochemistry of the West Carpathian alpine-type ultramafites. Náuka o Zemi, Veda, vyd. SAV Bratislava, Sér. geol., 12, 1-148.

Medveď, J., Plško, E., Cubínek, J. (1974): Studium der Zuverlässigkeit der spektrochemischen Methode zur Bestimmung von Mikroelementen in Silikatgesteinen, Acta geologica et geographica Universitatis Comenianae,Slovenské pedagogocké nakladateľstvo, Bratislava, Geologica Nr. 27, 183 –194.

Medveď, J., Plško, E. (1979): Spektrochemische Spurenbestimmung in ultrabasischen Gesteinen, Symposium über Petrogenese und Geochemie von geologischen Prozessen, Veda, vyd. SAV, Bratislava, 297-302.

Minczewski, J., Marczenko, Z. (1975): Chemia analityczna, Tom I, Państwowe wydawnictwo naukowe, Warszawa, p.189.

Ormándy, M. (1904): Ásványtan és chemia, Franklin – társulat, Budapest, p.170.

Ostroumov, G. V. (1979): Metodicheskie osnovy issledovania khimicheskogo sostava gornykh porod, ryd i mineralov, Nedra, Moskva, p. 4.

Plško, E. (1998): Problematika rozloženia zložiek v reálnych vzorkách, Zajištení kvality analytických výsledků, 2THETA, Český Těšín, 114-127.

Plško, E. (2000): Vývoj, súčasná náplň a možnosti hutníckej analýzy, 2THETA, Český Tešín, 9 – 18.

Treadwell, F. P. (1918): Kurzes Lehrbuch der analytischen Chemie, I. Band, Franz Deuticke, Leipzig und Wien, 544 p.

Slovak Geol. Mag., 9, 2 – 3(2003) 99 – 104

The Past, Present and Future of Atomic Spectroscopy in Chemical Analyses

KAROL FLÓRIÁN and *JÜRGEN HASSLER

Department of Chemistry, Faculty of Metallurgy, Technical University of Košice,
SK-042 00 Košice, Letná 9; *Wacker Ceramics, D-87405 Kempten, P.O.BOX 1526

Abstract. The DC arc excitation has played an important role (as the well-known spectrographic analytical technique) in the analysis of solid samples, first of all in specific area of geochemical analyses, for a long period. Unfortunately, in this time all possibilities of the optimisation of photographically registrated spectra were fully exploited and after the introduction of modern spectrometric techniques based on ICP excitation also in the field of solid sampling spectrometry the DC arc method lost its importance. The necessity of new, quick and simple methods has led to the comeback of the old DC arc spectroscopy. This situation was caused by some of their advantages, first of all the working temperature. The use of modern, computer-controlled equipment with exactly defined arc current/time programme gives a new design. On the other hand the connection of the spectrometer to the source by quartz-fibre optics is also a new instrumentation. In direct analysis of powder samples it is one of the successful ways for work without any additives in sample preparation. The electrothermal vaporization (ETV) is a well-known and powerful device for the sample introduction in optical emission spectroscopy. This timesaving, robust and precise method became more and more important in industrial laboratories as well as in science and research. In the meantime a nearly perfect commercial ETV-system is available and it represents in connection with an ICP-CID-spectrometer the future in the spectrochemical analysis of powders.

Key words: atomic emission spectroscopy, solid sample analysis, old-fashioned and modern methods, come back of DC-ARC, ETV-ICP-OES.

The past

The history of atomic spectroscopy goes back to the spectroscope (Fig.1), which has been used for first time by Bunsen and Kirchhoff in 1859 (Kirchhoff et al.,1860). For a long period of spectroscopic history the direct – current arc excitation has been the leading technique of direct analysis of powdered samples, first of all in specific area of geochemical analyses. This, first only semi-quantitative method, achieved after a long-year optimization and quantification (Zimmer et al.,1982) e. g. internal standard method, Lomakin-Scheibe equatation, blackening-transformation procedures, etc. the position of a quick, wide used multi-element quantitative method. The last optimization in evaluation of photographically registrated spectra using modern densitometers (Zimmer et al.,1982), have led to average precision of about 15 % with relatively low detection limits. Some modifications of the D.C.arc itself were also developed, at least the use of the stationary magnetic fields (Lummerzheim et al., 1969), inhomogeneous magnetic fields (Todorović et al., 1969), or the double-plasma method (Vukanović et al., 1977) should be mentioned. Also continuous sample introduction techniques (Fig. 2) were successfully evaluated and used in the practical analysis of powdered samples.

The intensive development of new excitation sources in atomic spectroscopy and commercial use of modern spectrometric techniques, which began in the half of the last century, has stopped the whole evaluation of mentioned old spectrographic technique. The research was consequently directed towards the use of solution methods, connected with the most successful excitation source of this period, the ICP.

The present

The development of spectrochemical methods is mainly prompted by three aims (Broeckaert et al.,1987): the improvement of the limit of quantification, the increase of the reliability of analytical information and the cost reduction – economical aspects. In most typical analyses of solid samples the direct analysis (solid sampling – analysis) seems to be an advantageous alternative to the usually preferred methods using wet digestion in sample preparation. The advantages are obvious, they are summarized (Bendicho et al.,1991; Schrön et al.,1997) as follows:

- reduced sample pre-treatment and hence, an increase in the speed of the whole analytical procedure,
- low contamination risk, an essential requirement when trace levels of metals are to be determined,
- fewer possibilities of analyte losses during the sample pre-treatment or retention of insoluble residues,
- the use of corrosive and hazardous chemicals is avoided
- very small material consumption.

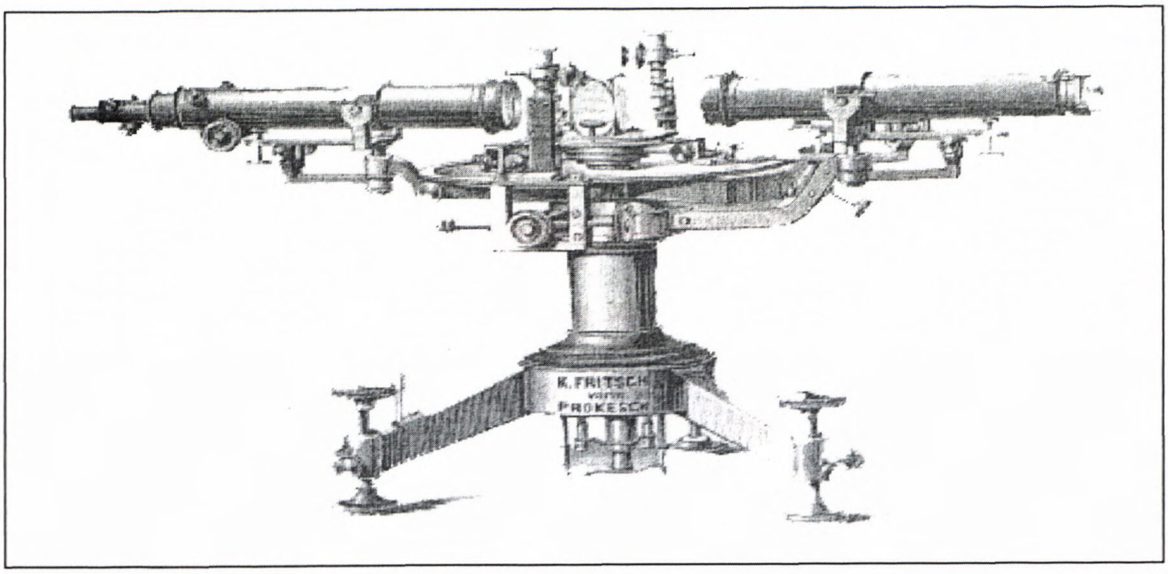


Fig. 1 The old-fashioned spektroscope

On the other hand, there are many of disadvantages to mention, just the most important (Schrön et al., 1997; Pauwels et al.,1991) of these:

- small range of the suitable reference materials (CRM-s),
- dosage problems caused by low sample weight (inhomogeneity),
- difficulty of independent and absolute calibration,
- difficulty connected with the direct-weighing method (inability to dilute samples, having analyte concentrations greater as the working range).

In the development of modern spectrometric methods of direct analysis of solids the attention was logically focused on the most succesfull excitation source in optical emission spectrometry (OES), the inductively coupled plasma (ICP). Besides the methods of direct sample introduction (Fig. 3): DSI-ICP (Blain et al.,1992) and slurry technique (Dočekal et al.,1992), the main attention was paid to the electrothermal vaporization systems (ETV), similarly to the technique applied in atomic absorption spectrometry (AAS), where many of alternative systems have been described and discussed in recent years (Kurfürst, 1998; Matusziewicz, 1986; Kántor et al., 1992; Golloch et al., 1995). It was stated, that because of the maximum temperature level of ETV at about 2900°C either the use of modifiers (Broeckaert et al.,1989; Nickel et al.,1995), or special working gas mixtures (Verrept et al.,1993; Kántor et al.,1992) is needed for the successful analyses of such typical materials, as advanced ceramic powders (e. g. SiC, B_4C, Si_3N_4, etc.) or other materials containing refractory elements.

On the other hand, the once successful solid-sampling technique – the D.C. arc evaporation and excitation source with higher evaporation and excitation temperature

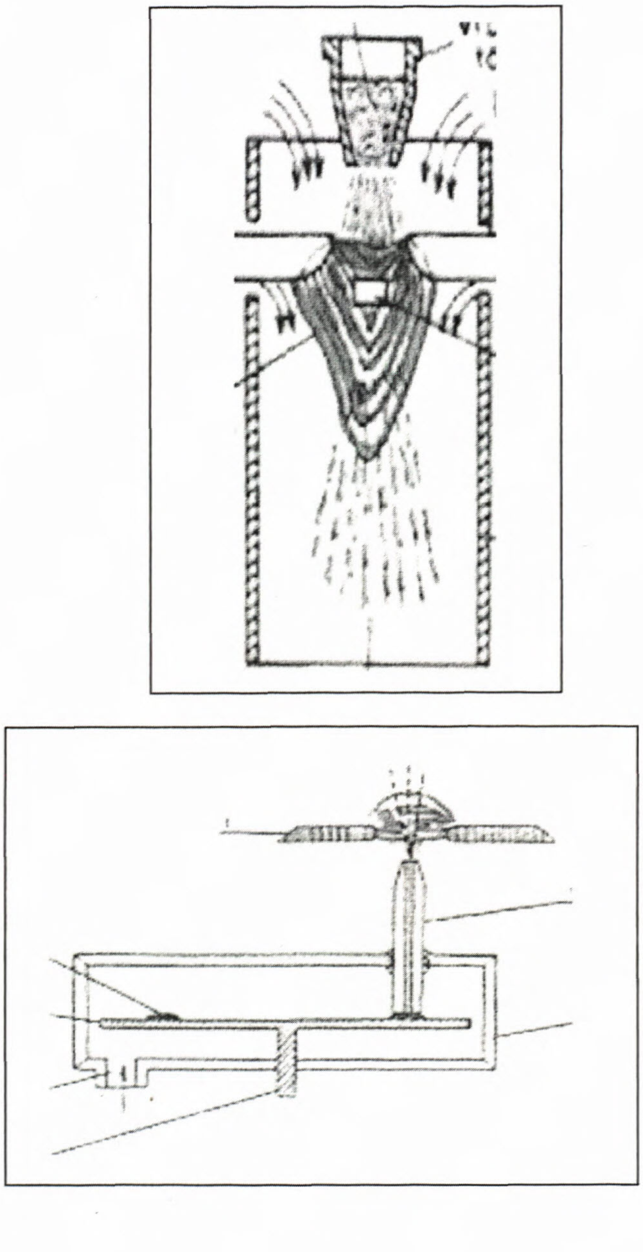


Fig. 2 Two typical continuous introduction systems of powdered samples

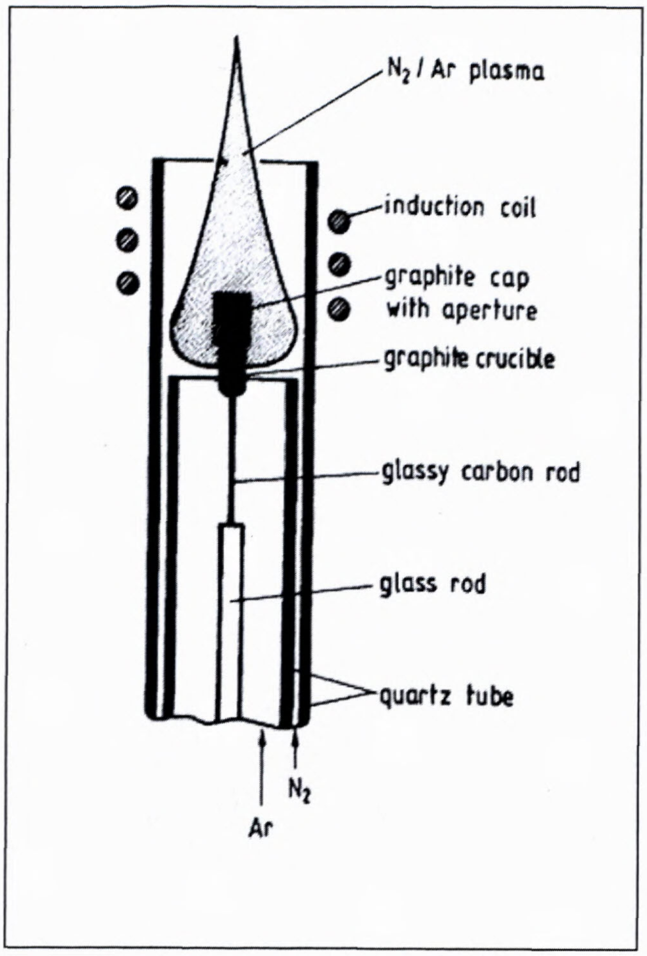


Fig. 3 Direct sample introduction system into ICP excitation source

(about 4000°C) was totally forgotten, first of all because of poor precision of old-fashioned spectrographic technique with photographic registration of spectra. In order to avoid the disadvantages of the old-fashioned DC-arc spectrography a new, electronically controlled DC arc was connected with the quarz-fibre optics to a multichannel spectrometer (Fig. 4 – an overview on electrode profile and the double-optics signal processing system) as a alternative method to the ETV-ICP and/or SS-ETV-AAS techniques in the routine analysis (Flórián et al.,1996).

The precision, reproducibility and long-time stability of the DC-ARC-OES method in SiC analysis should illustrate the data (Hassler, 2001) in the Table 1.

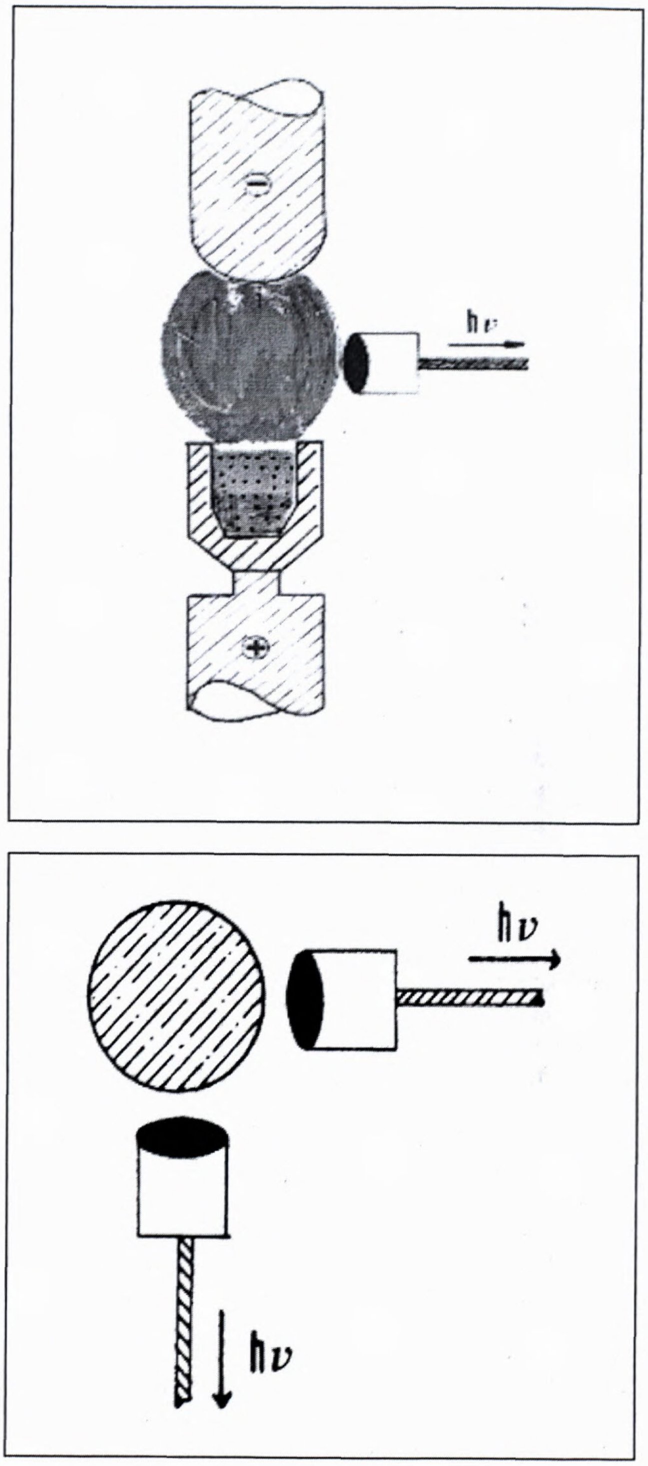


Fig. 4 The double optics signal processing system in connection with modernized DC-arc source

The future

Since many years a lot of effort has been taken to introduce solid samples directly into an ICP without dilution. Electrothermal vaporisation of powdered samples in a graphite tube and graphite boat and transfer of the aerosol via a tube connection to the plasma is one of the most interesting methods because of its precision and good reproducibility, its robustness and its easy and fast handling. It should be menshioned, that the idea of such sample evaporation, separated from the excitation process (Fig.5) goes back to the 40-ties of last century (Preuss, 1940). Following several laboratory concepts and own inputs a commercional state-of-the-art instrument has been developed (Hassler et al., 2002). Meanwhile its has become an important tool in a lot of industrial and research laboratories in both, routine analyses and research work. An integrated autosampler (Fig.6) with micro balance allows to work with excellent efficiency especially in industrial applications. For the ETV furnace a special gas-

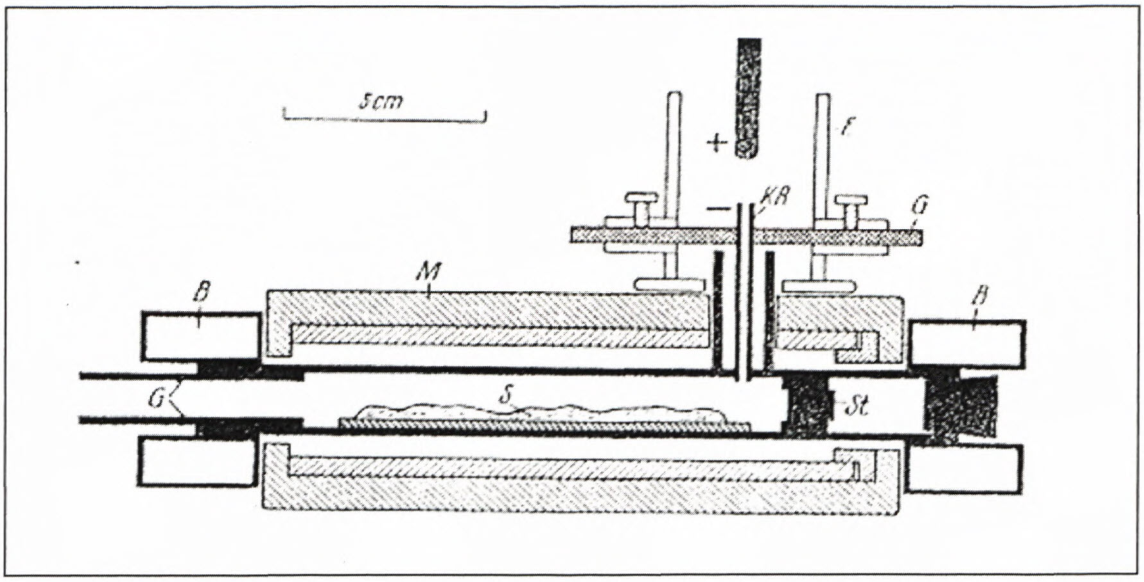


Fig. 5: The old-fashioned solid-sample evaporation and excitation system, proposed by Preuss

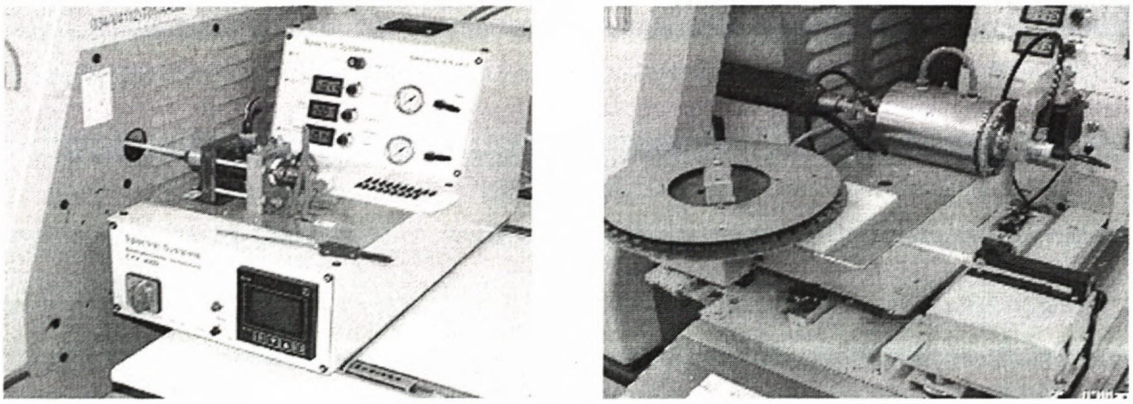


Fig. 6 The modern automatized ETV instrumentation

guide was developed which allows very high transport efficiencies and minimum memory effects. This is – among the robust, compact design and engineering – one of the main advantages against former concepts. Furthermore, the sample can be halogenised by a small amount of reaction gas in order to transform also the refractory elements into volatile halogenides. This lowers the vaporisation temperature and surpresses the formation of carbides. An integrated online-pyrometer measures and controlls the boat temperature, which allows the use of individual temperature programms via microprocessor control.

Some results (Hassler, 2001) of SiC analysis using the above described ETV-ICP technique and their comparison with results of solution ICP analysis as well as DC-ARC-OES analysis are summarized in the Table 2.

The common problem of all solid sampling spectrochemical methods is the adequate calibration. Mostly only a limited number of adequate certified reference materials (CRM-s), or laboratory reference materials (LRM-s) is aviable. Therefore besides the use of solution standards some other calibration procedures were proposed as the so called one-standard method. Here the change of independent variable – concentration is achieved by applying different weights of one standard. The comparison of the efficiency of both above mentioned calibration methods enable the validation characteristics of DC-ARC-OES analysis of BN and B_4C (Flórián et al., 2003) summarized in the Table 3.

The comparison of both studied calibration procedures shows their matrix dependence. While the results of BN matrix illustrate a good agreement in calibration parameters (a, b, r), in matrix B_4C are these quite different, in some cases more as one order of magnitude. Some further experiments with various matrices, more analytes and variable excitation conditions (to avoid the influence of excitation process) are needed. At least it is possible to declare the one-standard method as an possible alternative of calibration if none other ways are disposable.

*Table 1: The **RSD** (%) – values of 6 repeated measurements of 5 analytes in 4 SiC standards and 12 repeated series*

Element	Standard	Series											
		1	2	3	4	5	6	7	8	9	10	11	12
Al	**1**	4.5	4.5	6.6	6.0	5.1	5.2	5.8	7.5	4.6	8.4	4.1	5.4
	2	3.9	7.7	6.3	5.1	2.9	7.9	10.8	9.1	4.8	6.1	7.7	6.6
	3	5.0	4.8	3.9	5.7	5.0	5.8	6.2	7.4	3.5	7.5	5.7	5.7
	4	8.3	6.3	3.9	4.0	7.6	8.0	9.7	10.1	8.3	7.4	4.8	7.4
Fe	**1**	2.5	2.0	4.8	4.0	4.4	4.2	4.2	5.6	3.5	7.5	5.0	5.1
	2	2.7	4.6	2.4	3.2	1.5	4.3	4.8	8.6	1.5	3.7	3.0	4.0
	3	2.7	3.6	2.4	7.0	2.6	3.4	6.4	2.9	3.2	3.6	6.0	2.8
	4	5.3	5.8	6.4	5.2	3.9	2.4	5.7	11.4	7.2	6.5	6.6	4.3
Ni	**1**	4.7	2.5	10.8	6.1	6.4	5.4	6.4	8.1	8.5	13.2	7.7	7.9
	2	3.5	4.8	2.8	4.8	2.6	5.5	7.4	11.8	2.7	6.4	5.3	7.4
	3	4.6	3.2	5.6	8.4	4.6	4.5	9.1	6.6	2.6	6.4	8.2	5.6
	4	8.8	10.1	11.1	9.5	9.7	6.8	9.3	***17.9***	12.0	10.3	6.5	8.4
Ti	**1**	4.4	5.4	6.9	5.5	6.4	9.5	5.5	5.0	5.1	8.6	7.0	4.8
	2	4.8	6.7	6.2	8.3	4.5	8.7	6.6	10.7	4.5	8.4	6.0	9.1
	3	3.5	7.9	6.6	8.0	6.5	10.6	7.6	9.2	8.9	8.8	7.6	4.0
	4	8.6	9.6	7.8	9.8	7.8	4.7	10.2	11.9	8.5	6.9	6.9	5.7
V	**1**	5.0	5.7	7.3	10.1	7.1	8.1	6.3	10.1	6.5	8.9	4.0	6.4
	2	5.5	9.6	7.0	8.9	5.1	10.9	8.7	6.7	8.0	9.1	7.4	8.0
	3	7.8	7.8	8.8	9.1	7.0	10.1	6.3	7.5	10.9	10.4	7.2	9.7
	4	8.1	10.4	8.4	10.1	9.2	5.9	10.2	***15.0***	10.9	8.2	6.0	6.8

Table 2: Comparison of main validation characteristics of some analytes in SiC obtained using 3 different methods of spectrochemical analysis

Method	RSD / %					Recovery / %				
	Al	Fe	Ti	V	Zr	Al	Fe	Ti	V	Zr
solution ICP-OES	3.4	7.4	6.3	7.8	8.9	100	107	100	96	112
DC-ARC-OES	2.0	2.8	4.6	9.2		107	105	101	78	
ETV-ICP-OES	3.4	1.9	3.0	11.5	3.4	107	100	119	101	99

Table 3/a : The main characteristics of calibration functions (y = a + b . c) of Ca and Si in BN

Calibration parameter	Element			
	Ca		Si	
	5 LRM	single measur. n = 25	5 LRM	single measur. n = 25
concentration range / $\mu g.g^{-1}$	20 - 295	7 - 355	18 - 75	3 - 88
r	0.998	0.999	0.999	0.983
RSD_{method} / %	4.8	8.5	3.7	9.7
a	6.44 ± 0.950	6.71 ± 0.896	5.55 ± 0.180	5.63 ± 0.299
b	0.166 ± 0.0056	0.163 ± 0.0056	0.220 ± 0.0051	0.213 ± 0.0080

Table 3/b : The main characteristics of calibration functions (y = a + b . c) of Al and Fe in B_4C

Calibration parameter	Element			
	Al		Fe	
	4 LRM	single measur.	4 LRM	single measur.
		n = 15		n = 15
concentration range / $\mu g.g^{-1}$	35 - 100	6.8 - 100	580 - 1200	108 - 1500
r	0.994	0.929	0.999	0.971
RSD_{method} / %	5.7	17.8	1.3	14.3
a	6.36 ± 0.372	7.59 ± 0.512	37.7 ± 0.167	19.2 ± 2.98
b	0.074 ± 0.0047	0.140 ± 0.0115	0.023 ± 0.0005	0.055 ±0.0036

References

Kirchhoff, G. & Bunsen, R.: *Spectralbeobachtungen.* C. A. Lenoir, Wien (1860).

Zimmer, K., Flórián, K. & Heltai, Gy.: Progr. analyt. atom. Spectrosc., 1982, **5**,341 (and references cited therein).

Lummerzheim, D. & Nickel, H.: *Z. anal. Chem.,*1969, **245**, 267.

Todorović, M, Vukanović, V. & Georgijević, V.: *Spectrochim. Acta* 1969, **24 B**, 571.

Vukanović, D., Simić, V., Vukanović, V., Nickel, H. & Mazurkiewicz M.: Spectrochim. Acta 1977, **32 B**, 305.

Broeckaert, J. A. C. & Tölg, G.: Fres. Z. Anal. Chem. **326** (1987), p. 495-509.

Bendicho, C. & de Loos-Vollebrecht, M. T. C.: J. Anal. Atom. Spectrom. **6** (1991), p.353-374.

Schrön, W., Nimmerfall, G., Dressler, B. & Danzer, K.: Proceedings of XXX. CSI Melbourne (1997).

Pauwels, J., De Angelis, L. & Grobecker, K. H.: Pure & Appl. Chem. **63** (1991), p.1199-1204.

Blain, L. & Salin, E. D.: Spectrochim Acta **47 B** (1992), p.205-217.

Dočekal, B., Broeckaert, J. A. C., Graule, T., Tschöpel, P. & Tölg, G.: Fresenius J. Anal. Chem. **342** (1992), p. 113-117.

Kurfürst, U. (ed.): **Solid Sample Analysis.** Springer Verlag Berlin-Heidelberg (1998).

Matusiewicz, H.: J. Anal. Atom. Spectrom. **1,** (1986). p. 171-184.

Broeckaert, J. A. C., et al.: Fresenius J. Anal. Chem. **332** (1989), p. 825-838.

Verrept, P., Galbács, G., Moens, L. & Dams, R.: Spectrochim Acta **48 B** (1993), p.671-689.

Nickel, H. & Zadgorska, Z.: Spectrochim Acta **50 B** (1995), p.527-535.

Kántor, T., Záray, Gy.: Fresenius J. Anal. Chem. **342** (1992), p. 927-932.

Golloch, A., Haveresch-Kock, M., Platnikow-Vossgätter, F.: Spectrochim Acta **50 B** (1995), p. 501-516.

Flórián,K., Hassler, J. & Schrön, W.: Fresenius J. Anal. Chem. **355** (1996), p. 601-605.

Preuss, E.: Z. angew. Mineral. **1941**, 3, 8-20.

Hassler, J., Detcheva, A., Förster, O., Perzl, P. K. & Flórián, K.: Annali di Chimica **89** (1999). p.827-836.

Hassler, J.: PhD-Theses, TU Košice (2001).

Flórián, K., Hassler, J., Rutarová, P. & Záray, Gy.: Chem. Papers **57**, 151- 154 (2003).

Slovak Geol. Mag., 9, 2 – 3(2003),105 – 107

Research Methods of Atmospheric Solid Pollutants

ERIKA KRAKOVSKÁ[1], DAGMAR REMETEIOVÁ[1], JAROSLAV TOMKO[1] and DANIELA MACKOVÝCH[2]

[1]Technical University, Faculty of Metallurgy, Department of Chemistry, Letná 9, 042 00 Košice,
Slovak Republic, E-mail: erika.krakovska@tuke.sk
[2]Geol. Survey of Slovak Republic Bratislava, Geoanalytical Laboratories, Markušovská cesta 1, SK 052 40 Spišská Nová Ves

Abstract. Gravitation dust sediment, which surface of particles is enriched by volatile toxic elements in industrial sites, is created by particles, with diameter greater than 10 μm. The studied samples of the gravitation dust were collection near U. S. Steel s. r. o., so they represent pollutants of a metallurgy industry. In this place it is assumption of maximum amount of collected samples. Characteristics of gravitation dust were studied by various analytical methods and after determination of particles size these were applied for study of original samples and size fractions.

Phase composition of gravitation dust sediments was detected by three methods of qualitative analysis (thermal differential analysis, X-ray phase diffraction analysis and local electron microanalysis). The total content of major and trace elements was determined by methods of quantitative analysis after total decomposition of samples. The content of major elements was determined by atomic emission spectrometry with inductive coupled plasma after decomposition by HF, $HClO_4$ and HNO_3. The total content of matrix elements from this region decreases in the order Fe, Ca, Mg, Al, Mn. Other risk elements in samples occur on the trace level and their content decrease in the order Pb, Zn, Cu, Hg, Cd, Sb, Ni, Co. As and Sb was determined by atomic absorption spectrometry with hydride generation, Hg by atomic absorption spectrometry with thermal-oxidative generation and amalgamation after decomposition by aqua regia. Other elements by FAAS were determined.

Mobile and mobilizable element forms were determined by extraction with enable extraction agent. Extraction conditions were specified on the Košice-city sample and these conditions were applied for single step extraction of gravitation dust samples from the U. S. Steel region. For determination of mobile form of risk element samples were extracted by 0.1 mol NH_4NO_3 and for determination of mobilizable element forms by 0.1 mol.dm^{-3} EDTA. It was found, that in these samples elements in the dangers mobile forms consist mainly of Zn, Cd, Cu and in the mobilizable form of Cd, Zn and Cu.

The analyses of the acquired data from metallurgical industry region revealed that: applied research procedure enables to find complex data about characteristic of gravitation dust sediment; characteristic of gravitation dust sediment are significantly changing with specific region and single step extraction of dust enough inform about soils contamination.

Key words: gravitation dust sediments, fractionation, single-step extraction

Introduction

Dust particles in atmosphere of industry regions contain higher content of risk elements as dust particles of other regions. Toxic elements evaporated during high-temperature processes (such are e. g. combustion or metallurgical processes) have a trend to condense on surfaces of solid pollutants. Dust particles have a variety range size and from their size depend not only rapidity and way their removal from atmosphere, but their ecological impact to other environmental components too.

Gravitation dust sediment is created by particles with diameter higher as 10 μm, which are capable of spontaneous sedimentation. Its delay time in atmosphere is very short and its effect on living organisms is minimal. On this account the quantity of gravitation dust sediment is not able criteria for evaluation of situation of atmosphere pollution. The quantity of gravitation dust, which is expressed in g.m^2 in 30 days is related on the area of sedimentation and express of pollution extent of soils or vegetation. Particles, after its sedimentation, can contaminate soils by those toxic element forms, which are able of transport to the soil system. Consequently their biological mobility can enter from soil to food-chain a secondary contaminate living organisms.

For completely study of gravitation dust sediment can apply a lot of analytical methods, by help whom can study their physical and chemical properties. Our research program was concentrated on:

- determination of the particles size;
- determination of the major mineralogical composition in original samples and size fractions;
- determination of the total content of major elements in original samples and size fractions;
- determination of the total content of risk toxic elements in original samples and size fractions;
- determination of the content of risk elements in various physical – chemical forms (fractionation analysis) in original samples and size fractions;
- study of the pre-concentration method (SPE analysis) for directly risk elements determination in sorbet or elements determination after elution.

Research methods applied for study of atmospheric pollutants particles consisted especially from X-ray phase diffraction analysis, thermal differential analysis, local electron microanalysis, atomic absorption and emission spectrometry, roentgen fluorescence spectrometry and single step extraction by various extraction agents. By application of this methods were estimated necessary characteristics of atmospheric solid samples.

Results and discussion

The level of air pollution by solid particles has been monitored through concentration of fly dust couched in µg.m^{-3}. The overload of the highest admissible value of this concentration (60 µg.m^{-3}) in Košice region were registered on the monitoring station "Veľká Ida". This station occurs nearly of U. S. Steel s. r. o. (big metallurgical plant), which is the significant polluter of atmosphere in this region. The fly dust is created by particles, which diameter is less than 1 µm, with very small sedimentation power.

Gravitation dust sediment, which surface of particles is enriched by volatile toxic elements in industrial sites, which is created by particles, with diameter greater than 10 µm. The studied samples of the gravitation dust were collection near by U. S. Steel s. r. o., so that represented pollutants of a metallurgy industry. In this place it is assumption of maximum amount of collected samples. An overload of the highest admissible quantity of dust sediment (12.5 g.m^{-2} for 30 days) it was registered here in each season of 2002 year. The total amount of collected samples into 12 settling glass vessels in time 3 months was from 6 g to 14 g approximately.

The phase composition of gravitation dust sediments was detected by three method of qualitative analysis (thermal differential analysis, X-ray phase diffraction analysis and local electron microanalysis). It was detected, that the particles matrix is created mainly by $CaCO_3$, SiO_2, $Fe_3Al_2(SiO_4)_3$, Fe_2O_3 and MgO. The Fe is presents in the carbonate form too. From elements representative an environmental risk was detected presence of Cd in the carbonate form and Cu as malachite ($CuCO_3.Cu(OH)_2$) and otavite ($Cu_3(OH)_2.(CO_3)_2$). The presence of Ni, Co, Zn and Mg in carbonate forms was detected only partly. A part of elements is bound as oxides. The example of configuration and composition shows Fig. 1.

The total content of major and trace elements was determined by methods of quantitative analysis after total decomposition of samples. Samples by HF, $HClO_4$ and HNO_3 were decomposed and content of major elements by atomic emission spectrometry with inductive coupled plasma was determined. The total content of matrix elements from this region decreases in the order Fe, Ca, Mg, Al, Mn. Other risk elements in samples occur on the trace level and their content decrease in the order Zn, Pb, Cu, Hg, Cd, Sb, As, Ni, and Co. As and Sb was determined by atomic absorption spectrometry with hydride generation, Hg by atomic absorption spectrometry with thermal-oxidative generation and amalgamation after decomposition by aqua regia. Other risk elements by method of F AAS were determined.

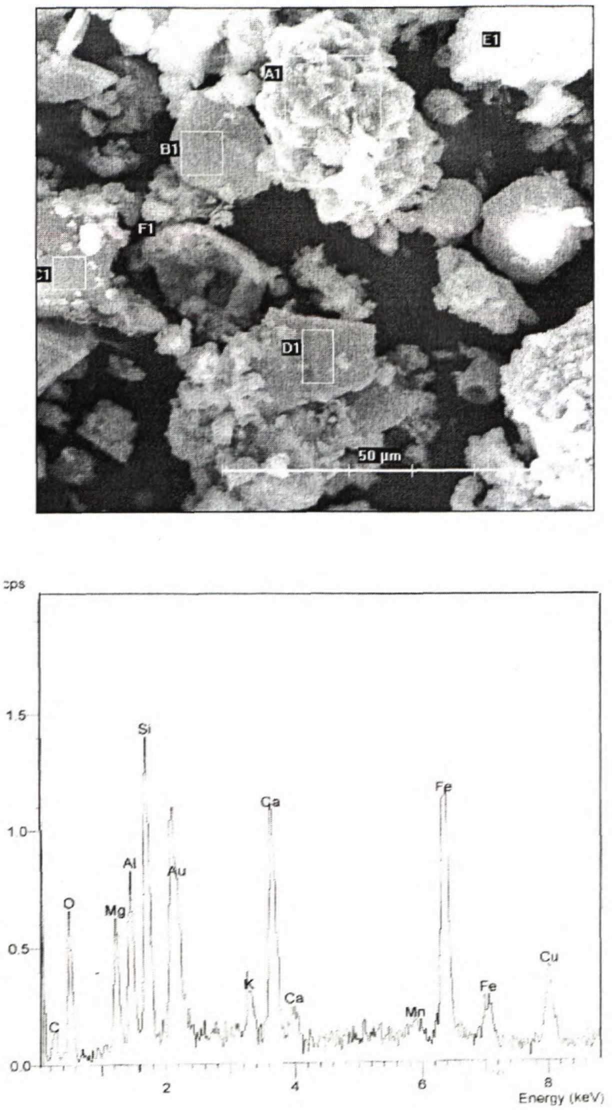


Fig. 1. The electron microscope picture and local element analysis of the dust particle (F1)

The fractionation is method used on the identification of element forms according to their various physical (solubility) or chemical (bonding) properties (Templeton et al., 2000). In the fractionation analysis of soils exist a lot of single-steps and sequential extraction procedures on the isolation of mobile and mobilizable element forms. From the standpoint of mobility in soil, the mobile forms (water-soluble and ion-exchangeable) constitute the highest danger. These forms are mobile in normal soil conditions. The mobilizable forms (mobile, organic, and carbonate) are mobile in changed soil conditions.

It is possible to applied of extraction procedures on samples of gravitation dust sediment in order to isolation of risk element forms, which are mobile from dust particles to soils. Application of money wise and time-consuming sequential extraction procedures for the dust samples is not necessary because dust particles have different matrix composition than soil particles. In the case of application of the single-step extraction is necessary regard the difference in amount of collected samples.

Table 1. The content of selected risk elements in gravitation dust sediment sample from locality Košice-Veľká Ida

Element		**Zn**	**Pb**	**Cu**	**Hg**	**Cd**	**Sb**	**As**
original sample	**weight %**	0.064	0.018	0.0063	0.0021	0.0004	0.0006	0.00041
d<36 µm		0.079	0.0224	0.0089	0.0025	0.0006	0.0006	0.00048
d>36 µm		0.053	0.0126	0.0056	0.0020	0.0004	0.00035	0.00037

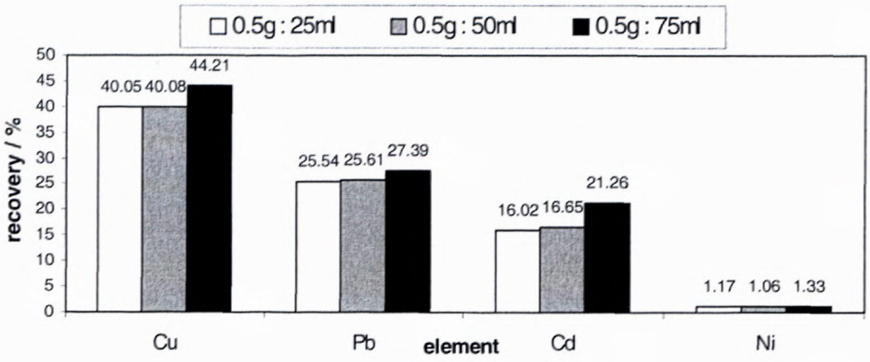


Fig. 2. The optimalization of extracting ratio for extraction by 0.05M EDTA.

For single-step extraction procedures following extracting reagents were used: distilled water, snow water, 0.1 mol.dm^{-3} $NaNO_3$, 0.1 mol.dm^{-3} NH_4NO_3, 0.1 mol.dm^{-3} $CaCl_2$ and 0.1 mol.dm^{-3} EDTA. By this reagents can extract mobile and mobilize element forms. In contrast of soil, we are applied the dust and the extracting ratio 1:150 (1g dust and 75 cm^3 extract agent). Other condition remained saved (Remeteiová et al., 2002). Extraction conditions were specified on the Košice-city sample and these conditions were applied for the single step extraction of gravitation dust samples from U. S. Steel region. For determination of mobile form of risk element samples were extracted by 0.1 mol NH_4NO_3 and for determination of mobilizable element forms by 0.1 mol.dm^{-3} EDTA. It was found, that from selected elements in dangers mobile forms are binding mainly Zn and Cd, and in the mobilizable forms Cd, Pb, Zn, and Cu.

Table 2. The percentage of selected risk elements in mobilizable forms.

Percentage / %	**Zn**	**Pb**	**Cu**	**Cd**
d<36 µm	48.3	65.1	39.5	81.2
d>36 µm	61.8	82.4	48.9	76.1

Because concentration of risk elements in extracts often is very low, we search possibility to find the able preconcentration method. We applied SPE extraction (solid phase extraction) and we are tested column from two various producers. Pre-concentrated risk elements can determine directly of sorbets by roentgen fluorescence spectrometry, or by analysis of pre-concentrated elute by other spectroscopic methods.

Conclusion

In consequence of acquired data from metallurgical industry region we can state that:

- applied research procedure enables to find complex data about characteristic of gravitation dust sediment particles;
- characteristic of gravitation dust sediment particles expressively changed with concrete region;
- single step extraction of dust sediments enough inform about soils contamination;
- spectroscopic methods provide relevant data information.

Acknowledgement

This work is a part of Grant Project of Slovak Republic, VEGA No. 1/0386/03.

References

Templeton, D. M., Ariese, F., Cornelis, R., Danielsson, L. G., Muntau H., van Leeuwen, Łobiński R.: Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methological approaches. IUPAC Recommendations 2000, Pure Appl. Chem., Vol. 72, No. 8, 1453-1470, 2000.

Remeteiová, D., Krakovská, E., Tomko, J., Sminčáková, E. & Vojteková, V.: Extrakcia vzoriek prašných spadov EDTA, sborník přednášek "Mikroelementy 2002", 124-128, 2002.

Slovak Geol. Mag., 9, 2 – 3(2003), 109 – 113

Electrothermal Evaporation in ICP-OES; Its Development and State-of-the-art Nowadays

JÜRGEN HASSLER and *PETER R. PERZL

Wacker Ceramics, D-87405 Kempten, P.O.BOX 1526
*Spectral Systems, D-82256 Fürstenfeldbruck, Augsburger Strasse 37

Abstract. ETV-ICP-OES is a well established method nowadays. It is defined as a separate on-line tandem configuration for sample introduction. In graphite furnace a sample is being evaporated and transformed into a dry aerosol by gas phase condensation. This aerosol is being transported to the ICP-torch.

For to achieve satisfying results a lot of innovative research and development work on the furnace design itself, but also for modifier application and temperature control was necessary. Modern power-supply-electronics and microcomputer-control made compact instrumentation possible.

ETV-ICP-OES combinations using special resistance heated graphite furnaces turned out to be one of the best established and dominating method in solid sampling. Commercial solid-state automated systems are available and have proved their suitability in industrial routine labs as well as in numerous research laboratories.

In the meantime a lot of interesting applications have been carried out, one of them will be presented at the end of this article.

Key words: Solid sampling; electrothermal evaporation; ETV-furnace, ETV; ETV-ICP-OES;

Introduction

Electrothermal evaporation systems (ETV) have been object to research and develop-ment for several decades. The idea always was fascinating indeed to analyse solid samples directly without any dilution process with all its problems, possible contaminations and time consumption.

The History of ETV

The history of electrothermal vaporisation starts (Fig. 1) with the Lokyer-furnace in the 70th of the 19th century (Lokyer 1878).

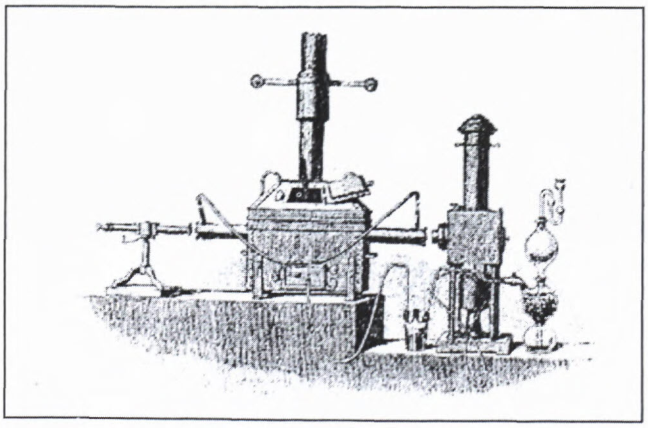


Fig. 1. Lokyer-furnace 1878

Lokyer observed phenomena of atomic absorption at his instrument. The atomiser con-sisted of a coal-heated iron-tube. Hydrogen was used as protection gas, generated by a Kipp generator.

The first real application of an ETV was done by Preuss (E. Preuss 1940). He developed an ETV-device to vaporise easy volatile metals in geological samples to analyse these elements in a DC-Arc. The coupling was made by a tube connection directly to the upper arc-electrode, shaped as a Graphite tube.

Numerous ETV-designs were derived from developments in AAS-furnace systems. So H. Massmann (Massmann 1966) may be considered as the father of graphite-tube ETV-devices and T.S.West (West 1969) as the one of the bridges-, filament- or coil- types. In the beginning of ICP-OES the ETV in first instance was meant as alternative to the sample introduction systems (nebulizers) working not satisfying at that time. By this point of view also the works of A. Fassel (Nixon at.al. 1974) concerning the evaporation by a Tantalum-filament and G. F. Kirkbright (Kirkbright at.al. 1979) concerning an ETV-device using a carbon-bridge were performed. As final stage of the graphite-bridge-furnaces the ETV-system of A.Golloch and M. Haveresch-Kock (Golloch at.al. 1990) may be considered, an ETV using a graphite-bridge and graphite-boats for high weights.

A parallel development of the graphite-bridge-type was the direct connection of the furnace to the aerosol-tube of the torch.

It was started by K. Ohls and B. Hütsch (Ohls et al., 1985) with their first experiments with a direct coupling partly by open funnel-shaped connecting parts.

It was continued by M. Reisch (Reisch et al., 1989) and for the time being finished in a technically advanced way by H. Nickel and Z. Zadgorska (Nickel et. al., 1993) by a ETV-unit with pneumatically operated furnace and direct compound with the aerosol tube.

Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava 2003 ISSN 1335-096X

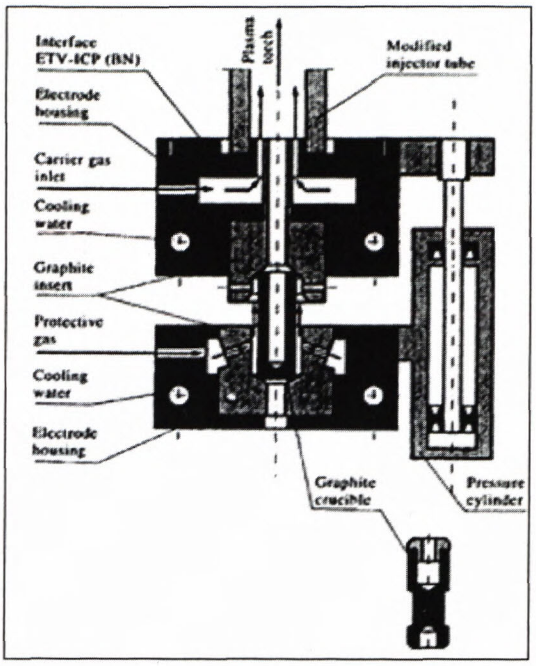


Fig. 2: pneumatic ETV-device Nickel, Zadgorska 1993

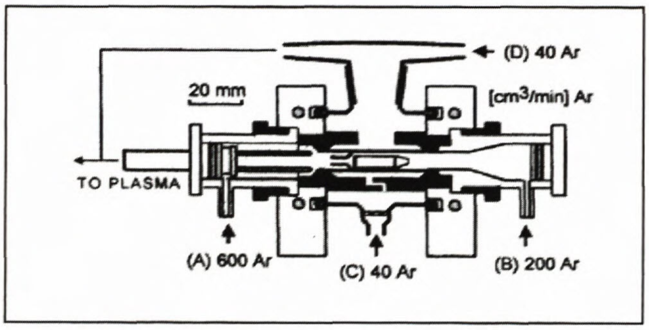


Fig. 3: Kantor-Zaray end on ETV-furnace 1992

In later phases ETV-ICP-OES configurations with graphite tube furnaces mostly used converted AAS-graphite-furnaces from Perkin Elmer for example HGA 74 (Aziz et al., 1981).

Less numerous but at least even successful were adaptations of the solid-sample-AAS-furnaces manufactured by Grün-Optik. (Schäffer et al., 1998).

Decisive pre-works for the development of the commercial ETV-System ETV 4000 (Spectral Systems) were done by T.Kantor and G.Zaray with their modified ETV-furnace (Kantor et al., 1992).

Based on this furnace in several stages of development and by numerous improvements the most modern ETV-system today was created (Hassler et al., 1999).

Development and state of the art of ETV-4000

The furnace based on the Kantor/Zaray-design is a longitudinally resistance heated type in end-on configuration. This means that a graphite tube of about 8mm diameter and 41mm length is heated by an electrical current of up to 400 Amps while a gas flow is being guided through the tube from one end to the other. The sample, that may be solid, dried liquid or dried slurry, is placed on a separate graphite support, a so called boat, in the hot centre of the heating graphite tube. The recleaned boat can be reused many times.

Halogenation: For evaporation high-boiling or carbide forming elements in many cases very high temperatures of more than 2500 °C are necessary. However, for a reasonable life time of the graphite tube the maximum temperature is limited to 3000°C and heating cycles normally should not exceed much more than 2500°C. To overcome this problem in the literature the addition of modifiers like PTFE-powder, carbon tetrachloride vapor or halocarbons has been described. Oxides and carbides by this addition are being transformed into volatile halides (Kantor, 2001). In the described system Freon 12 (CCl2F2) or Freon 22 (CHClF2) are used. These gaseous modifiers are continuously led over the sample while the evaporating process together with the carrier-argon in a con-centration of about 0.5 to 1.5%. So they are present all the time of heating and especially at higher temperatures, in contrary to solid or liquid modifiers, which evaporate and decompose at a certain temperature, mostly between 400 and 1000°C.

Transport efficiency: A transport as complete as possible of the produced aerosol into the ICP-plasma is essential for high efficiency of the process. It has been found that most of the transport losses occur in the first few millimetres downstream the end of the graphite tube. Also the end of the graphite tube itself that is hold by cooled graphite brackets and therefore cooler than the centre of the tube is affected by vapour losses. To overcome this problems a special design of this area was necessary.

A tube in tube construction was developed which the smaller inner tube (nozzle) ends some millimetres outside the end of the heating tube. The evaporated sample flows together with the carrier gas through the nozzle which is hold and connected to the hottest area in the centre of the heating tube and thereby always keeps a relatively high temperature. The end of this nozzle is separated from the end of the alumina transport tube by an alumina transition ring. A ring-shaped gap is formed between the end of the nozzle and the beginning of the transition ring. In this gap an additional argon stream is be-ing introduced (by-pass gas) that forms a boundary layer at the inside of the transport tube shielding it from the hot sample vapour. At the same time both streams are continuously being mixed and a supersaturated relatively cold aerosol is being formed. Additionally, the carbon particles originating from the decomposed Freon help to form condensed aerosol particles. This is an additional important benefit of the halogenation. The flow-relation between both argon streams is electronically controlled and adjustable by MFC´s. So under optimised conditions transport efficiencies of 80% can be achieved.

Temperature control: A graphite tube normally has a life time of several hundreds of cycles. It is clear that by sublimation losses, but also by an in-situ pyrolytic coating caused by the Freon the wall thickness and thereby the electrical resistance and the thermal behaviour of the tube are changing. To get reproducible temperatures a

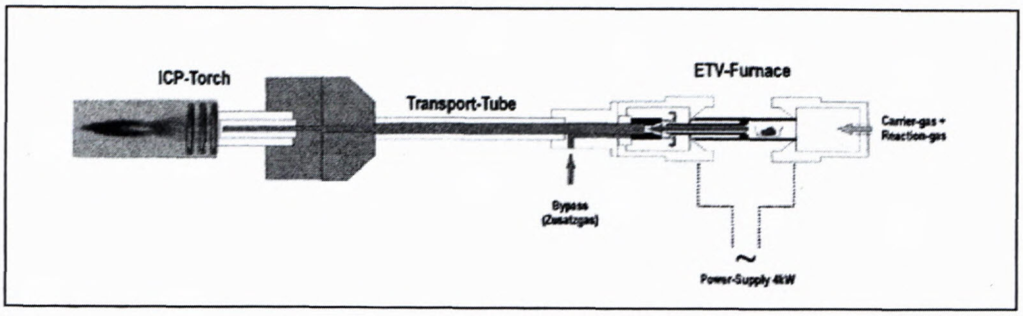


Fig. 4: ETV - ICP – connection

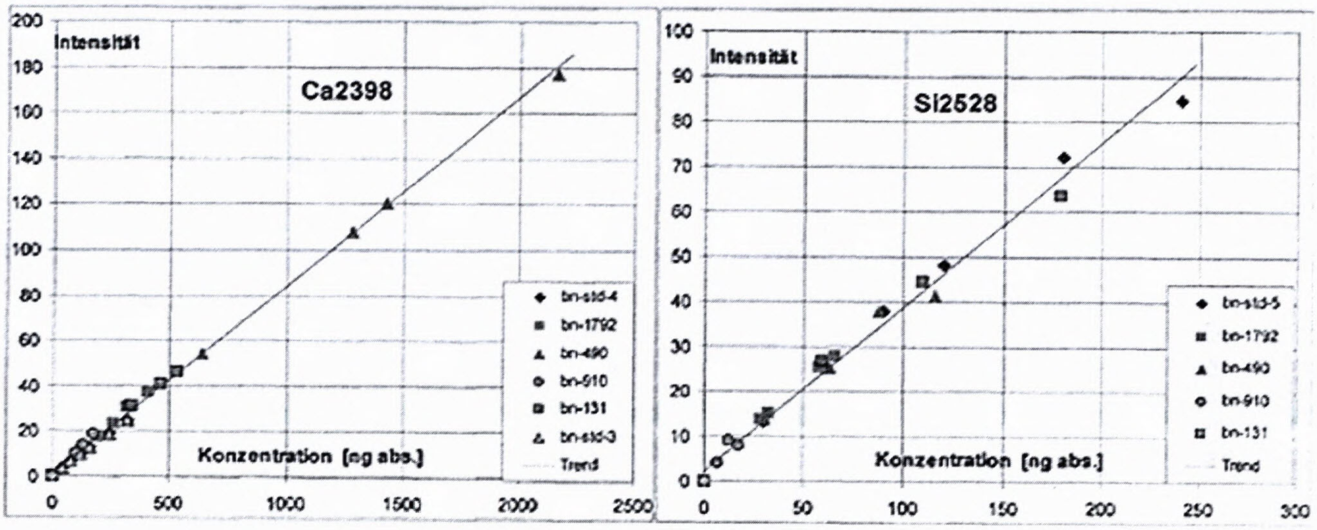


Fig. 5: Calibration functions of Ca and Si for BN-routine analysis

miniature pyrometer was developed to record the temperature of the sample-boat. It was observed that the boat temperature differs essentially from the temperature of the outside of the graphite tube (up to 500°C) so that it is necessary that the pyrometer looks directly onto the boat. The pyrometer is integrated into the control-circuit of the electrical power-supply of the furnace and therefore provides together with the PID-control not only constant temperatures independent from the furnace conditions, but also a fast and precise setting of different temperature levels by the program controller without over-shootings. The temperatures controlled by the pyrometer range between 20°C and 3000°C with a precision of 2%. The furnace thereby allows optimum and reproducible temperature steps for ashing and evaporation of low- and high-boiling elements, and even speciation analysis is possible.

Automatisation: In industrial routine analysis today with hundreds of samples time becomes more and more precious. So the modern laboratory equipment needs to be as automated as possible. For this purpose the ETV-system is equipped with an auto-sampler that is able to handle magazines with 10 or 50 boats automatically. An integrated microbalance is also available. The system is connected to the spectrometer by an interface, so that a stack of max. 50 samples can be run fully automatic.

Experimental results

The experimental results were found by routine analysis of Boron Nitride.

Hexagonal Boron Nitride is a white powder that because of its similarity with graphite in its crystal-structure and its characteristics of lubrication is also known as "white graphite". Boron Nitride is inert against water, doesn't react with acids and acid-mixtures and is not perfused by metals, metallic and non metallic slags. Boron Nitride has a very high temperature-stability in reducing gas-streams up to approximately 2400°C. Furthermore, it is resistant until 1800 °C against carbon and until 700°C against chlorine-gas. It is oxidation-resistant and has a good thermal conductivity. Boron Nitride is an electric insulator in contrast to graphite.

The shown calibration functions in figure 2 (concentrations see table 1) for Ca and Si demonstrate as an example for all other elements the simplicity and high quality of the calibration in the routine analysis of BN by ETV in a relatively large concentration range.

For quality control and statistical evaluation for routine analysis of BN a special analytical procedure was established.

Table 1: Concentrations of calibration standards (BN-home standards) [µg/g]

	fluid std	bn131	bn490	bn910	bn1792
Ca	40	145	732	55,5	127
Si	30	56	49	6,2	19,5

Table 2: Results of the evaluation of 85 runs

Element	set point [µg/g]	actual value [µg/g]	s [µg/g]	RSD [%]
Ca	145	148,1	4,7	3,2
Fe	17,5	16,4	1,3	7,5

Table 3: statistical results

	Dried standard solution				BN - home standard bn910			
element	c ng/µl solution	BM a=001	CCM a=001	RSD_{meth}	c µg/g BN-STD	BM a=001	CCM a=001	RSD_{meth}
Al3082	1	0,101	0,4	1,8	1,8	0,165	2,131	12,2
Ca2112	2	3,005	2,728	4,9	55,5	2,531	10,102	1,9
Cu3247	0,5	0,012	0,318	2,9	0,1	0,049	0,399	41,2
Fe2338	2	0,427	0,671	1,5	3,6	0,638	3,213	9,2
Mg2798	0,5	0,259	0,587	5,3	8,2	0,192	1,713	2,2
Si2528	2	2,678	1,983	4,5	6,2	4,622	3,526	5,9
Zr2734	1	0,166	0,778	3,5	0,5	0,185	0,4	8,3

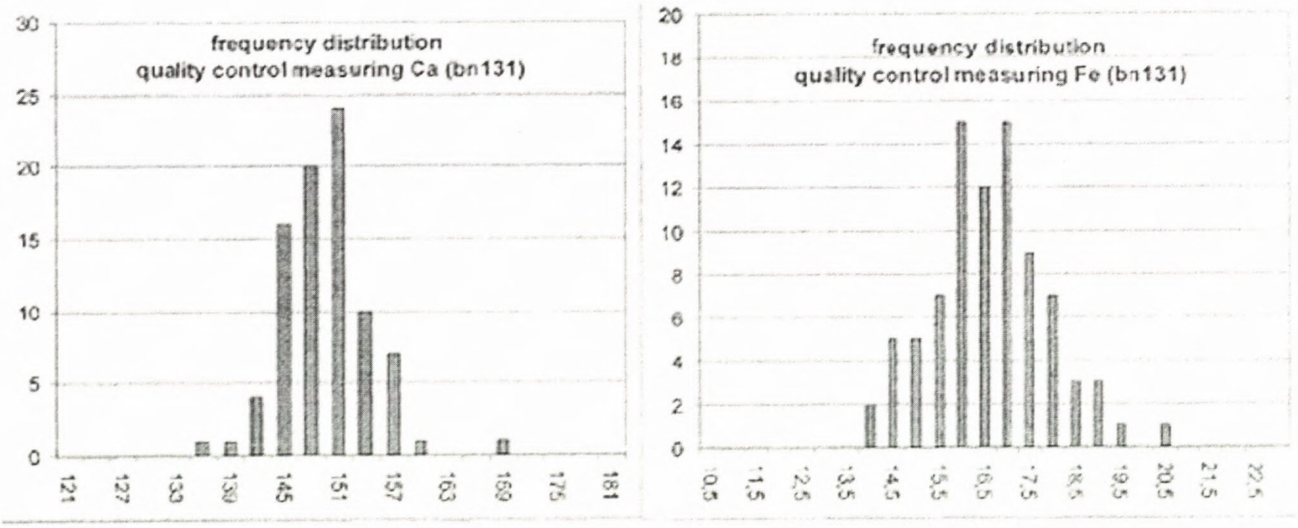


Fig. 6: Frequency distributions of Ca and Fe for 85 single results

For each analysis run of a completely provided 50-boat-sampler 20 boats are used for standards: dried standard solution (6 x) plus 4 BN home-standards (4 x bn1792, 4 x bn490, 3 x bn910, 3 x bn131). The remaining positions normally are used for 10 samples (3 x each).

After the analysis run the measurements are evaluated with an excel-program. As results the calibration functions (graphical and numerical) and statistical data (e.g. mean values, SD, RSD) of standards and samples are presented.

The standard bn131 which is included in the calibration is additionally evaluated like an unknown sample. The results of Ca and Fe (85 runs dated from 01. 03 – 07. 03) are presented as frequency distributions (concentration µg/g).

In table 3 are shown statistical results of the method for some elements/lines like limits of detection (blanc method, BM, calibration curve method, CCM, according to DIN 32645) and RSD_{method}. The values are very convenient for the demands of routine analysis of Boron Nitride.

Conclusion

A modern state-of-the-art ETV-system enables the user to achieve very short analysis times, especially with solid samples, and thereby a significant reduction of analysis costs. Further a reduced calibration expenditure is possible (standards, SRM's or home-standards). The method allows good reproducibility depending on the sample with RSD values of 2-10%. The high transport efficiencies of up to 80% provide high limits of detection (5 - 0.005 ng abs.). Of course by the high sensitivity also clean room conditions are essential for best results.

The highly automated systems (auto sampler) are also easy to handle (maintenance) and rather robust. The field of applications is extremely wide. Some examples, where the authors have own experience with are: Si_3N_4, SiC, BN, B_4C, graphite, coal, oxides (Al_2O_3, SiO_2), sediments, sludges, plant material, apple leaves, river-cancer, green algae, milk powder (Iodine), hair samples, plastics (electric cables). Further applications are organic and inorganic slurries, tissues, blood, environmental samples, all kinds of biological samples or food, speciation analysis, volatile heavy metals, homogeneity tests. All these applications demonstrate the wide field for practical ETV-ICP analysis. Today the method is well established in numerous industrial as well as in research labs and continuously gets increasing importance in practical analytic work.

Literature

Lockyer, J. N. *Studies in Spektrum Analysis*; Appleton: London, **1878**.

Preuss, E. *Z. angew. Mineralogie* **1941**, *3*, 8-20.

Massmann, H., Berlin 1966; Akademie Verlag; 297-308.

West, T. S.; Williams, X. K. *Anal. Chim. Acta* **1969**, *45*, 27-41.

Nixon, D. E.; Fassel, V.A.; Kniseley, R.N. *Anal. Chem.* **1974**, *46*, 210-213

Kirkbright, G. F.; Snook, R. D. *Anal. Chem.* **1979**, *51*, 1938-1941

Golloch, A.; Haveresch-Kock, M.; Fischer, W. G. *GIT Fachz. Lab.* **1993**.

Ohls, K.; Hütsch, B. *ICP Inform. Newsl.* **1986**, *12*, 170-176

Reisch, M.; Nickel, H.; Mazurkiewicz, M. *Spectrochim. Acta* **1989**, *44 B*, 307-315.

Nickel, H.; Zadgorska, Z. *ICP Inform. Newsl.* **1993**, *19*, 71-73.

Aziz, A.; Broekaert, J.A.C.; Leis, F. *Spectrochim. Acta* **1982**, *37B*, No. 5, 369-379.

Schäffer, U.; Krivan, V. *Anal. Chem.* **1998**, *70*, 482-490.

Kántor, T.; Zaray, G. *Fresenius J. Anal. Chem.* **1992**, *324*, 927-935.

Hassler, J.; Detcheva, A.; Förster, O.; Perzl, P. P.; Florian, K. *Annali di Chimica* **1999**, *89*, 827-836.

Kántor, T. *Spectrochim Acta* **2001** 56 B 1523-1563.

Slovak Geol. Mag., 9, 2 – 3(2003), 115 – 117

Possibilities of Mössbauer Spectrometry in Geology and in Environmental Science

MARCEL MIGLIERINI

Department of Nuclear Physics and Technology Slovak University of Technology, Ilkovičova 3,
812 19 Bratislava, Slovakia, e-mail: bruno@elf.stuba.sk

Abstract. Basic principles of Mössbauer spectrometry are briefly summarised with special emphasis put on hyperfine interactions and their relation with spectral parameters. Qualitative and quantitative analysis enables determination of crystallographic phases present in the sample and determination of stochiometry, respectively. Using the latter, oxidation states of iron via determination of Fe(II)/Fe(III) ratio can be obtained. Unique features of Mössbauer effect technique which provide simultaneous information on structure and magnetic state of the resonant atoms are effectively applied for the usage of this method in geology and also in environmental science. Some illustrative examples are discussed to more details. An importance of Mössbauer spectrometry is underlined by its involvement in extraterrestrial missions.

Keywords: Mössbauer spectrometry, hyperfine interactions, phase composition

Mössbauer spectrometry

Mössbauer spectrometry provides simultaneous information about structural arrangement of the resonant atoms and their magnetic states. Both can be unveiled from deviations in the positions of nuclear energy levels which sensitively reflect influence of hyperfine interactions. The latter are governed by location of the resonant atoms in particular crystalline sites, their oxidation state, coordination number, site symmetry, etc. The type and the number of the nearest neighbours should they be constitution element, substitutional ligands or even impurities and/or lattice defects play a crucial role. As a result of the above mentioned effects, electric and magnetic moments are present and they cause splitting of nuclear energy levels. As demonstrated in Fig. 1, characteristic types of Mössbauer spectra and their respective spectral parameters are observed which can be directly correlated with particular hyperfine interactions.

Mössbauer spectrum parameters of crystalline systems are discrete values. They can be, similar as fingerprints, unambiguously assigned to various structural positions of the resonant atoms. Positions of lines provide information on the intensity of hyperfine magnetic field B or on the tensor of electric field (derived from the spectral parameters called quadrupole splitting – D) at the nuclei as well as on the density of electron cloud inside the nucleus (isomer shift – d). Linewidths are proportional to structure (defects, ordering) and line intensities (line areas) give the orientation of the net magnetization. Line area of the particular spectral component is directly proportional to the relative number of resonant atoms in that particular structural positions which grants a quantitative analysis or determination of stochiometry of the investigated sample.

Mössbauer Spectrometry in Geology

At present, about 47 elements featuring nearly 110 transitions can be used for the observation of the Mössbauer effect and, in turn, for spectroscopic purposes. However, almost 65% of scientific papers in this field are devoted to the usage of the isotope of iron ^{57}Fe (Mössbauer Data Center, 2003). Because iron is widely abundant element in geological species, too, application of Mössbauer spectrometry in geology is straightforward.

The diagnostic potential of Mössbauer spectrometry can be effectively utilised in the determination of magnetic and non-magnetic lattices. Typical materials in this respect are magnetic oxides and magnetic fractions of minerals, intermetallic compounds and other materials interesting from the technological viewpoint. Especially in magnetically ordered minerals, Mössbauer parameters can be ascertained for each sublattice individually. Subsequently, individual moments, magnetic ordering temperature as well as magnetic structure can be identified (Lipka, 1999). Typical example is shown in Fig. 2 where a transmission Mössbauer spectrum of magnetite is displayed. It can be decomposed into two subspectra that belong to atoms positioned in tetrahedral and octahedral crystallographic sites. A comparison with a Mössbauer spectrum of metallic iron points out significant quantitative differences between these two examples as far as the hyperfine field value is concerned even though the same type of hyperfine interactions (magnetic dipole) applies.

Mössbauer spectrometry provides a simple means of quantitative measurement of the distribution of iron among its oxidation states, e. g. Fe(II)/Fe(III) ratio, based on the magnitude of isomer shift and quadrupole splitting. At the same time, qualitative analysis is also possi-

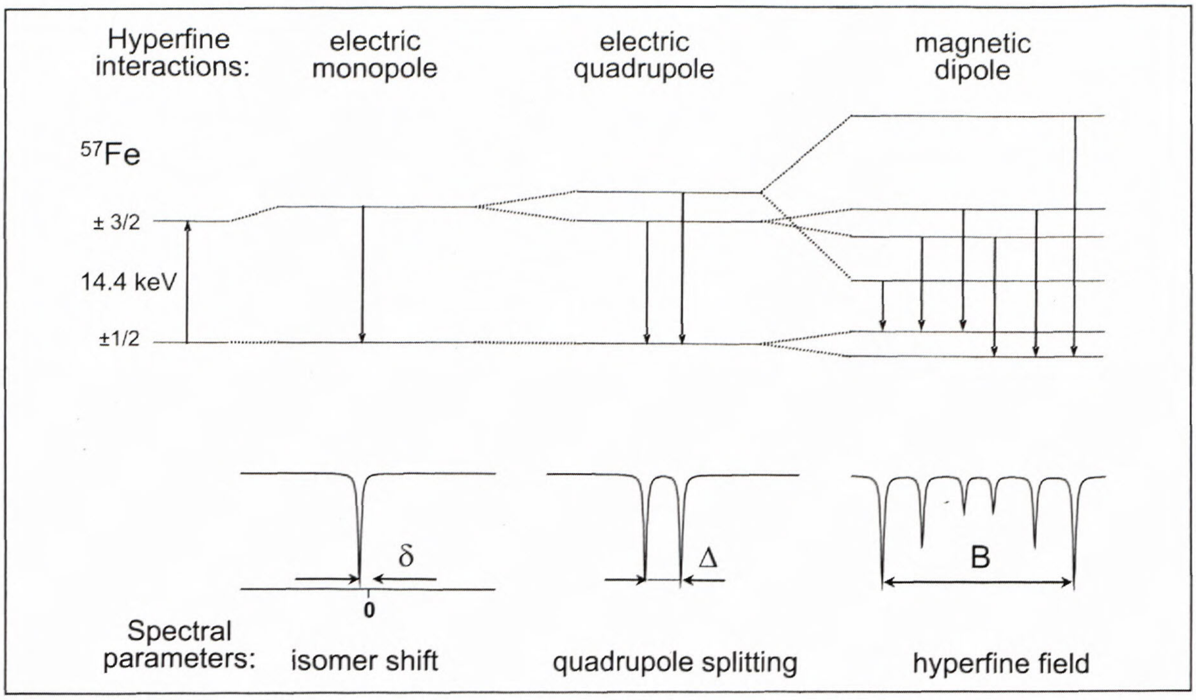


Fig. 1. Hyperfine interactions for ^{57}Fe nuclei and their influence on the shape of Mössbauer spectra.

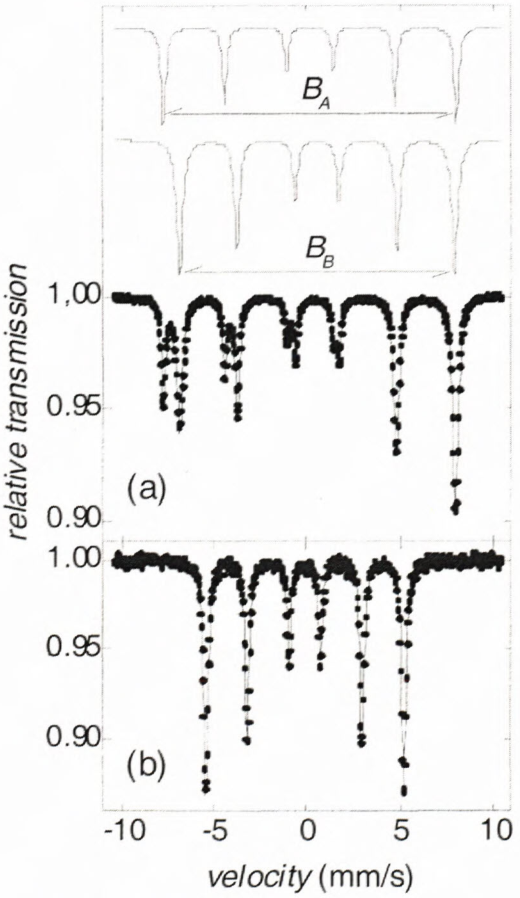


Fig. 2. Room temperature transmission ^{57}Fe Mössbauer spectra of (a) magnetite (Fe_3O_4) decomposed into spectral components: A – tetrahedral (B_A = 49.4T) and B – octahedral (B_B = 45.8T) sites of iron ions; (b) natural iron (B = 33.1 T).

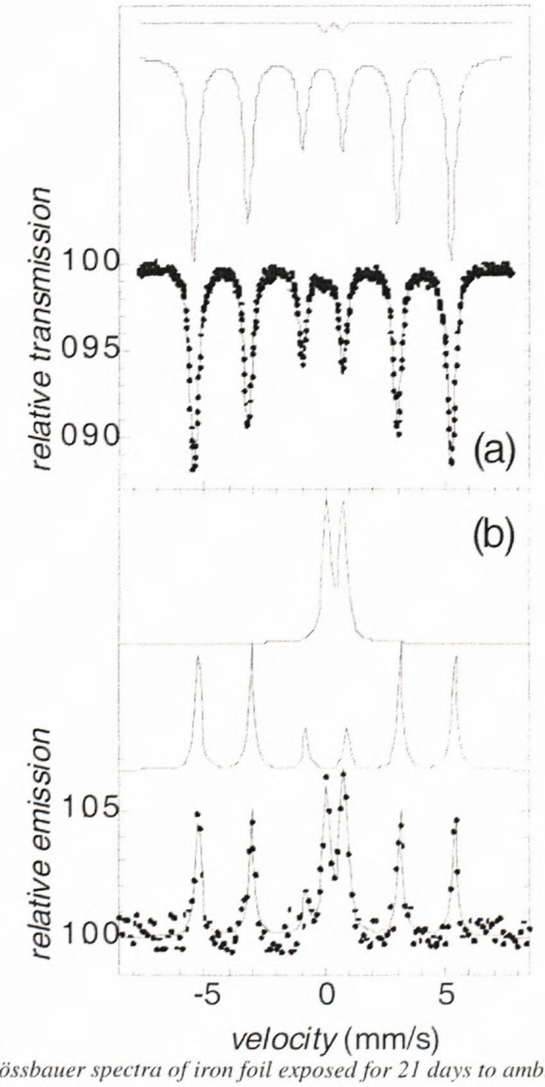


Fig. 3. Room temperature transmission (a) and emission (b) ^{57}Fe Mössbauer spectra of iron foil exposed for 21 days to ambient atmosphere in industrial urban area including spectral components (see text).

Mössbauer Spectrometry in Environmental Science

Crystalline α-Fe is a basic absorber for ^{57}Fe Mössbauer spectrometry. Its hyperfine parameters are well known and some of them are used to calibrate the experimental apparatus. Consequently, such material can be employed for environmental studies. Changes in bulk and to higher extent those of surface sensitively reflect the effects of environmental conditions.

Example of air monitoring with the help of Mössbauer spectroscopy is documented in Fig. 3. Calibration α-Fe foil (thickness of 25 μm) was exposed for 21 days to ambient atmosphere on a territory of a huge urban agglomeration. As a result, iron oxides were created.

Classical transmission geometry experiment showed only minor perturbation of the resulting Mössbauer spectrum (Fig. 3a) which was collected from a sample positioned in a vicinity of an industrial plant. It consists of two components: sextet of Lorentzian lines attributed to α-Fe substrate and a doublet which represents iron oxides induced by atmospheric conditions. Contribution of the latter is about 6%. Then we have applied conversion electron Mössbauer spectrometry (Miglierini and Seberíni, 2000) which is sensitive to resonant atoms located in surface regions to the depth of ca. 100 nm. Emission Mössbauer spectrum of conversion electrons in Fig. 3b unveiled that surface regions consist to almost 38% of oxides. Sextet of spectral lines belongs to the foil itself, i. e. α-Fe crystalline substrate.

Evaluation of samples placed in industry free areas disclosed lower amount of oxides on their surface which suggests smaller impact of atmospheric conditions on their formation.

Conclusions

Iron is one of key elements in the evolution of our planet. The identification and determination of iron bearing minerals, their weathering products, Fe(II)/Fe(III) ratio, and properties of magnetic phases can contribute to the understanding of chemical and physical processes in geology and environmental science. In this respect, Mössbauer spectrometry contributes significantly. Its unchangeable role is documented by the fact that Mössbauer spectrometers were mounted on board of space rovers which were launched in June 2003 for Mars missions (Mars exploration rover, 2003). It is foreseen that iron-bearing minerals such as carbonates, phyllosilicates, hydroxyoxides, phosphates, oxides, silicates, sulphides, sulphates, etc. including those that are magnetically ordered could be identified. The obtained data would help in the characterisation of the present state of Martian surface. In this way the possibilities of Mössbauer spectrometry in geology are extended also to extraterrestrial applications.

Acknowledgement

Financial contribution of the grant KEGA 3/100503 is acknowledged.

References

Web page of Mössbauer Effect Data Center: http://www.unca.edu/-medc/Statistics.html.

Lipka, J.: *Mössbauer Spectroscopy in Mineralogy and Geology* in: Mössbauer Spectroscopy in Materials Science, eds. M. Miglierini and D. Petridis, Kluwer Academic Publishers, 1999, The Netherlands, p. 97-106.

Mars exploration rover web page: http://athena.cornell.edu/the mission/-ins moss.html.

Miglierini, M. & Seberíni, M.: *Conversion Electrons – A Way to Study Surface Crystallization*, in: Proc. 6th Int. Workshop on Applied Physics of Condensed Matter, APCOM 2000, Kočovce, Slovakia, 19.-21.6.2000, p. 84-87.

Slovak Geol. Mag., 9, 2 – 3(2003), 119 – 122

Modern Electroanalytical Methods in the Analysis of Environmental Samples

ERNEST BEINROHR and ALENA MANOVÁ

Department of Analytical Chemistry, FCHPT STU Bratislave, Radlinského 9, 812 37 Bratislava
e-mail: beinrohr@chtf.stuba.sk

Abstract. The principles of flow-through coulometry with porous electrodes are listed in the paper. These electrodes enable a simple determination both of extremely low and high concentrations of electrochemically active species. Low analyte concentrations are measured by making use of stripping coulometry consisting of two principal steps: The analyte species are electrochemically deposited first and the galvanostatically stripped whereas the stripping chronopotentiogram is obtained. Higher analyte concentrations can be measured by making use of in-electrode coulometric titrations.

Key words: flow-through coulometry, trace analysis, coulometric titrations, porous electrodes

Flow-through coulometry has became a useful tool not only for scientific research (Tab. 1) but has been intensely used for routine analysis for various samples as well. The principles and experimental background of this method have been known since long but it was considered as a method for the measurement of main components in the samples which significantly hindered its utilisation for trace analysis. Coulometric measurements possess a very high sensitivity which is due to the measurement of electrical charge consumed during the electrolysis and the high value of the Faraday´s constant:

$$Q = z F n \qquad (1)$$

Q electrical charge
z charge number of the electrode reaction
n amount of the species electrolysed.

Notwithstanding the intrinsic high sensitivity of coulometry, it has rarely been used for trace analysis and in specialised laboratories only.

The measurement of consumed electrical charge during electrolysis can easily and reliably be measured. Moreover, there is no technical problem to measure charges as small as μC and nC corresponding to amounts of *nmol* and *pmol*. Hence, coulometry is in principle suitable also for the measurement of extremely low analyte concentrations. The main limiting factor is, that we cannot measure directly the net Faradayic current corresponding to the electrochemical conversion of the species of interest just the total charge consisting also from the background charges, capacitate charges. In the case that these components would be comparable with the net faradayic charge, the results would become unreliable due to the fact, that the net Faradayic charge is obtained as the difference between the total charge and the sum of all background charges, which may be obtained for example from the blank measurement.

The background signal can be minimised by using suitable electrode materials and optimum measurement parameters. Porous electrode materials based on glassy carbon and reticulated vitreous structure (reticulated vitreous carbon – RVC, Fig. 1) have proven their usefulness for this purpose [1]. The average diameter of the pores in the electrode should correspond to the thickness of the diffusion layer (approximately 5 – 50 μm). Here, if applying a constant current, the concentration of the electrolysed species will be virtually the same in the bulk of the electrode and the potential of the electrode will be governed by the Nernst-Peters equation, at least for reversible systems. Hence, the potential of the porous electrode will be given by the ratio of the activities of the oxidised and reduced forms of the treated species. Actually, the electrochemical changes proceed in the diffusion layer only and therefore these processes will proceed fast and exhaustively. Irregular pores in the electrode facilitate the formation of turbulences in the flowing solutions which enhances the mass transfer and correspondingly the effectiveness of the electrolysis from flowing solutions.

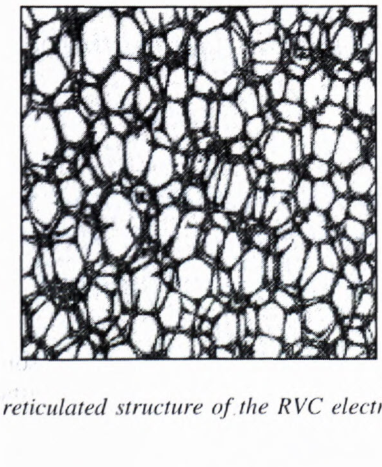


Fig. 1 The reticulated structure of the RVC electrode material

Table 1. Electroanalytical methods based on porous electrodes

Method	Signal	Relationship	Symbols
Hydrodynamic voltammetry	I vs E	$I_{lim} = R\,z\,F\,c\,v_{flow}$	R: recovery v_{flow}: flow rate
Galvanostatic flow-through coulometry	I vs t	$I = R\,z\,F\,c\,v_{flow}$ $Q = \int I dt = R\,z\,F\,c\,V_{sample}$	V_{sample}: Injected sample volume
Potentiostatic stopped-flow coulometry	I vs E	$Q = \frac{1}{e} \int I dE = R\,z\,F\,c\,V_{electr.\,bulk}$	e: potential ramp $V_{electr.\,bulk}$: Effective electrode volume
Galvanostatic stopped-flow coulometry (in-electrode coulometric titration – IECT)	dt/dE vs E	$Q = I \int \frac{dt}{dE} dE = R\,z\,F\,c\,V_{electr.\,bulk}$	I: Current E: Potential Q: Charge
Potentiostatic stripping coulometry	I vs E	$Q = \frac{1}{e} \int I dE = R\,z\,F\,c\,V_{sample}$	z: Charge number F: Faraday´s constant
Galvanostatic stripping coulometry (IECT)	dt/dE vs E	$Q = I \int \frac{dt}{dE} dE = R\,z\,F\,c\,V_{sample}$	c: Concentration

Owing to the above properties of porous electrode materials, they seem to be suitable for the measurement of low as well as high concentrations of electrochemically active species and species which can be converted to an electrochemically active form.

As the measurement mode for porous electrodes, the galvanostatic chronopotentiometry in coulometric mode has been found appropriate [2]. Here, the porous electrode serves as a generator as well as indicator electrode. As mentioned above, the potential change of the electrode corresponds to the change of the oxidised and reduced forms of the treated species during the electrolysis. The total volumes of the pores in the electrode gives the volume of the electrolysed solution, which is in fact the volume of the „titration vessel". The analyte species are titrated by constant current and the end point is indicated by a sudden change of the potential of the porous electrode. The duration of the titration is in fact the chronopotentiometric transition time τ. Knowing the void volume of the porous electrode V_{el}, the analyte concentration c can easily be extracted from the Faraday´s laws of electrolysis:

$$c = I\,\tau/(z\,F\,V_{el}) \qquad (2)$$

I applied current

τ chronopotentiometric transition time

This method – In-Electrode Coulometric Titration – is appropriate for measurement of analyte concentrations from about $10^{-5} – 10^{-7}$ mol/l, which is given by the lowest electrical charge (about 1 μC) which can be distinguished from the background charges of porous electrodes.

The sensitivity can significantly be enhanced by deposition of the analyte species from the flowing sample solution [3, 4]. Here, the porous electrode will also serve as a preconcentration device. Of course, this approach can only be applied for species which form solid deposits on the electrode surface such as metals, non-soluble compounds. The deposit is then stripped by constant current and the corresponding chronopotentiogram is recorded. Again, a coulometric titration is taking place, for the deposit is in fact titrated with electrical charge until oxidised or reduced quantitatively. The end of the titration (stripping) is indicated by a sudden change of the potential of the porous electrode. The concentration of the analyse can be obtained from the following equation:

$$c = I\,\tau/(z\,F\,V_{vz}) \qquad (3)$$

where V_{vz} denotes the sample volume taken for the deposition. Since this volume is usually 10 to 200 times larger as the void volume of the porous electrode in Eq (2), the lowest attainable concentration will be correspondingly lower as well – down to $10^{-7} – 10^{-9}$ mol/l.

The typical applications of flow-through coulometry with porous electrodes can be listed as follows:

Acid-base titrations

Determination of acids through reduction of H^+ ions to hydrogen

Determination of bases through oxidation of OH^- ions to oxygen

Redox titrations

Measurement of Cr(VI) through reduction to Cr(III)

Measurement of Fe(II), Fe(III) or total Fe

Measurement of dissolved oxygen

Determination of nitrates through catalysed reduction to ammonia

Determination of phosphates by making use of molybdates

Sulphate measurement through precipitation with barium chromate

Precipitation titrations

Determination of halogenides on silver coated electrodes

Complexometric titrations

Measurement of complexation capacities of waters

Trace and ultratrace analysis

Flow-through stripping coulometry for the determination of metals (As, Pb, Hg, Cd, Ni, etc.)

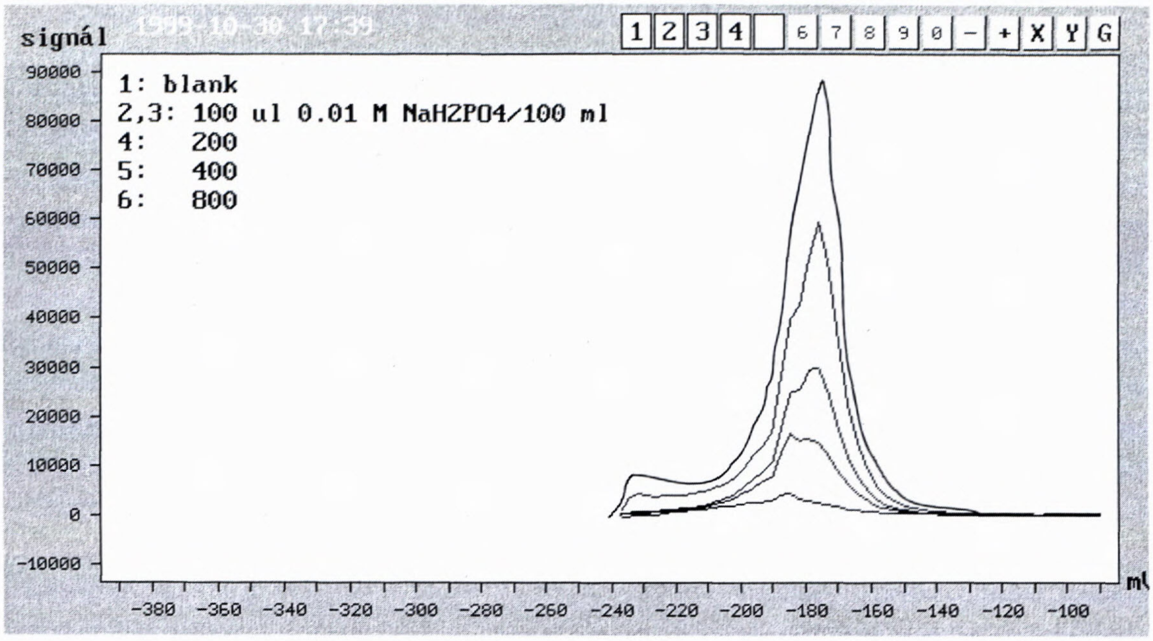


Fig. 2 Chronopotentiogram of phosphate in the presence of molybdate (obtained on EcaFlow Model 150, Istran, s.r.o., Bratislava).

Unattended monitoring
Monitoring of waters for metals
Monitoring of tap water for Fe and Mn

In Fig. 2 there is a chronopotentiogram obtained during the in-electrode coulometric titration of phosphate ions in water after addition of molybdate solution. Here, the formed heteropoly acid is electrochemically reduced to the „molybdenium blue“ form giving a typical reduction peak. Owing to the high charge number (up to 12) the measurement exerts a high sensitivity. Since not the colour is measured, turbid and/or coloured sample solutions can be analysed without interferences.

References

1. E. Beinrohr, M. Németh, P. Tschopel & G. Tolg: Design and characterisation of flow-through coulometric cells with porous working electrodes made of crushed vitreous carbon. *Fresenius J. Anal. Chem.* **343**, 566-575, 1992.
2. D. Jagner & A. Granelli: Potentiometric stripping analysis. *Anal. Chim. Acta* **83**, 19-26, 1976.
3. E. Beinrohr, P. Csémi, F. J. Rojas & H. Hofbauerová: Determination of manganese in water samples by galvanostatic stripping chronopotentiometry in a flow-through cell. *Analyst* **119**, 1355-1359, 1994.
4. E. Beinrohr, M,

Slovak Geol. Mag.,9, 2 – 3(2003), 123 – 124

The Analysis of Rare Earth Elements by Mass Spectrometry Method

TIBOR GÁL[1] and ALŽBETA HEGEDŰSOVÁ[2]

[1]Department of Physik, [2]Department of Chemistry of the Constantin Philosopher University,
Tr. Andreja Hlinku 1, 949 74 Nitra

Abstract. To perform a comprehensive analysis of the whole periodic system with low limits of proof, the spark source mass spectrometer has been used.

After examination of lantanoid containing geological samples based on qualitative analysis we can conclude, that rare earth determination makes more difficult by the presence of clusters with weight number equivalent to some of lantanoid group elements. Such interference effects can be caused by barium oxide and carbide ions, which are often contained in geological materials.

On the other hand, the presence of double ionified atoms of lantanoids is favourable, since it is a unique proof of the rare earth content.

Key words: rare earth elements, lantanoid, mass spectrometry

In recent two decades, the interest in the rare earths has increased in both practical life as well as in scientific research. Their research is challenging and requires the use of appropriate analytical methods. From practical point of view the preferred methods are those based on the atom nucleus properties, as the mass spectroscopy and the neutron activation analysis (NAA). For general lantanoid analyses the mass spectroscopy with spark ion source is applicable. In our research we solve two main problems: superposition of cluster ions and concentration dependence of analyse results.

According to the atomic mass number, various isotopes of lantanoids are partially overlapping, but each of the elements has one or two isotopes which can not be confused with any other element or isotope with the identical mass number.

Some difficulties are caused merely by superposition of ion clusters, particularly oxides and carbides of barium (Cornides, 1982; Cornides, Gál, 1978). The occurrence of superposition is especially counteracting the analysis, if it overlaps the bands of mono and polyisotopic elements, which are being analyzed (Tab.1).

Tab.1 Ions caused superposition.

Mass number	Overlaped ion	Overlaping ion
146	Nd^+	$^{134}Ba^{12}C^+$
147	Sm^+	$^{135}Ba^{12}C^+$
151	Eu^+	$^{135}Ba^{16}O^+$
159	Tb^+	$^{135}Ba^{12}C_2{}^+$
161	Dy^+	$^{137}Ba^{12}C_2{}^+$
166	Er^+	$^{134}Ba^{16}O_2{}^+$
167	Er^+	$^{135}Ba^{16}O_2{}^+$
169	Tm^+	$^{137}Ba^{16}O_2{}^+$

The possible method for elimination of quantitative errors is the separation of bands (Dietre, Becker, 1982; Oláh, Cornides, 1986). To prevent superposition problems we utilized equipment with high differentiating ability (10000).

The second approach is uses the doubly ionized atoms. In the case of lantanoids our measurements (based on the mass spectra of six different samples) showed that their occurrence is approximately the same as the occurrence of single ionized atoms (Tab. 2).

Tab. 2 The ratio of exposition for single- and double ionifed atoms.

Element	**La**	**Ce**	**Pn**	**Nd**	**Sm**	**Eu**	**Gd**
A^+/A^{2+}	1.3	1.2	1.8	1.5	1.2	1.9	1.3
	0.3	0.6	0.5	0.7	0.6	0.9	0.4
	1.1	-	1.3	1.4	1.9	2.2	0.9
	0.8	-	1.1	1	1.1	0.9	0.5
	1.4	-	1.8	1.5	1.4	1.2	0.8
	1.1	-	1.1	1.1	1.3	1.2	0.9
average	**1**	**0.9**	**1.25**	**1.2**	**1.25**	**1.4**	**0.8**
Element	Tb	Dy	Ho	Er	Tm	Yb	Lu
A^+/A^{2+}	1.3	1.4	1.4	1.5	0.5	0.6	1.2
	0.4	0.8	0.9	0.8	1	0.9	0.6
	1.2	2.4	1.1	1.2	1.6	1.6	0.8
	0.8	0.8	0.8	1.3	0.8	1.1	0.8
	0.7	1.3	1.1	1.5	0.5	1.2	1.1
	1.4	1	0.9	1.2	0.8	1.4	1.2
average	**0.95**	**1.3**	**1.05**	**1.25**	**1.1**	**1.15**	**0.95**

The differences result from the fact that double ionization depends to the high extent on the spark plasma conditions.

For one sample 20 – 30% differences for each element have been found and the average of averages is 1.1. In the case of double ionized atoms the result is more convenient then in the case of single ionized atoms, where 3 .... 30A^+/A^{2+} values have been found. Since the ratio from the ion cluster was min 100, the superposition in the spectra of doubly ionized rare earths can be eliminated by using the isotopes with the odd atomic mass number. The effect of concentration on the results of analyze is still not resolved. To some extent our observations may be considered as model experiments.

Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava 2003 ISSN 1335-096X

The mass spectroscopy analysis was repeatedly measured for samples of rare earth concentrations 500, 50, 5 and 0.5 ppm. Indium was used as the internal standard. According to our results, the relative sensitivity changes with different concentrations, but differences in concentration area 5 –500 ppm have not exceed 25%. The variations of sensibility with respect to concentration were not proportional.

The dispersion of the results is acceptable since it is known that the size of particles of rare earth in geological formations is ≈10 μm, and the homogeneity can not be increased according to ones needs.

Reference

Cornides, I. (1982): Mass Specrom, Ion. Phys. 45. 219.
Dietre, H & I., Becker, S. (1982): ZFI Mitteilungen Nr. 57.
Cornides, I. & Gál, T. (1978): High Tempr. Sci, 10.
Oláh, R. & Cornides, I. (1986): Mass Spectros. 34.

Slovak Geol. Mag., 9, 2 – 3(2003), 125 – 127

Analytical methodologies for Aluminium Speciation in Environmental Samples – a Review

JANA KUBOVÁ, VLADIMÍR STREŠKO and PETER MATÚŠ

Comenius University, Faculty of Natural Sciences, Mlynská dolina, 842 15 Bratislava, Slovak Republic

Abstract. In this paper the briefly overview on analytical methodologies for Al speciation in environmental samples are given. The advances of the different methods for quantitative determination of Al species during last decade are emphasized. Hyphenated techniques (coupling of HPLC/ FPLC with ICP MS/ ETAAS/ ICP AES, etc.) are currently the primary tool for species-selective analysis of Al. The advantages and limitations of the most used methods and the state of the art are pointed. The principal problem connected with Al speciation in environmental samples is absence of suitable certified reference materials for validation of used methods and procedures.

Key words: aluminium species, chemical and physical speciation, fractionation, hybrid techniques

Introduction

Aluminium toxicity is recognized as a serious global problem. Numerous research papers are published every year on the environmental effects of this element. Al is the third most abundant metal in the earth´ s crust, which comprises approximately 8% Al by weight. Because of its low solubility in solution under neutral conditions, Al was regarded as a non-toxic element. During the last two decades, however, it has been found that acid deposition leads to considerable increases of dissolved Al concentrations in acidified soil and surface waters. Elevated concentrations of Al can result in forest decline, reduction of agricultural productivity, and the death of aquatic organisms and fishes. Uptake of Al by man via different routes (food, tap water, water in Al utensils and dialysate) might cause serious neurotic diseases, e.g. Alzheimer´s disease, Parkinson´s disease, dialysis encephalopathy, osteomalacia, and anaemia. All of these make the determination of Al important.

Determination of total dissolved Al has a little environmental and biological relevance because the different Al species differ greatly in toxicity. It has been indicated by laboratory bioassay that monomeric inorganic Al^{3+}, $AlOH^{2+}$, $Al(OH)^{2+}$ and probably $AlSO_4^+$ are the most toxic forms, whereas Al-F and Al-Org can reduce or diminish toxicity. It is well known that free Al^{3+} occurs mainly below pH 4, labile complexed Al, e.g. $AlOH^{2+}$, $Al(OH)_2^+$, AlF^{2+}, AlF_2^+, and $AlSO_4^+$ are dominant in the narow pH range between 4 and 5, the amount of $Al(OH)_4^-$ increases rapidly from pH 5 to 8 (Sposito, 1996). The purpose of this paper is to review advances in analytical methodologies for Al speciation in environmental samples.

Analytical methods for the determination of aluminium species

The existing methods can be classified e.g. according to the principles used:

1. Methods based on size exclusion

Filtration, ultrafiltration and dialysis can be used to physically separate soluble aluminium from fine colloidal polymeric aluminium and aluminium bound to the macromolecular structures of humic and fulvic acids. Dialysis membranes commonly have pore diameters of 1 to 55 nm, ultrafiltration membranes have pore diameters ranging from1 to 15 nm, filtration from 0.1 to 0.45 µm. Speciation using dialysis and ultrafiltration must be done very carefully to avoid the potential problems which are connected with possible contamination from material of membranes, potential problem of changes in pH value during dialysis or reduction the quantity of dialyzed Al from solution of high organic matter content.

2. Application of single and sequential extraction

The utilization a number of single extractants (e.g. KCl, $CaCl_2$, EDTA, $K_4P_2P_7$, $CuCl_2$, $LaCl_3$) for determination of different forms of Al e.g. in agriculture, soil science etc., is known many years (Beckett, 1989).

Sequential extraction procedures are widely applied to soils and aquatic sediments to characterize their chemical phase associations but a little is known their application for Al. Determination of Al and other elements in certified reference materials using the optimized BCR sequential extraction procedure is publicated in Sutherland et al., 2002 and Kubova et al., 2003.

3. Methods based on kinetic or binding strength discrimination

One of the most frequently used strategies for Al fractionation is based on the different reaction kinetics of Al species with selective complexing agents, such as 8-hydroxyquinoline, pyrocatechol violet, aluminon, ferron, etc. (Clarke et al., 1996). By using short reaction times we can discriminate between „free“ and complexed aluminium. The chelants react more rapidly with toxic Al species as Al^{3+}, and $Al(OH)^{2+}$ than with other species as labile Al complexed by weak inorganic and/ or organic ligands and non-labile Al complexed by strong organic ligands. Reactive Al species in acidic soils from localities Nálepkovo and Banská Štiavnica (Slovakia) by kinetic discrimination were determined using „oxin" reaction with subsequent MIBK extraction (Dlapa et al., 2002).

Separation of different Al species can be realized by re-equilibration in the presence of chelants where the reaction time or contact time between chelants and Al is not deliberately controlled. This method is denoted the thermodynamic method. It is widely applied to the differentiation of Al species because many chelants are available and the equilibrium constants of the reaction between chelants and Al^{3+} are readily obtained by potentiometric titration (Clarke et al., 1996). The disadvantages of these methods are that the all these chelants can complex with many cations e.g. the coexistence of those cations (especially Fe^{3+}) with Al can also lead to an overestimation of toxic Al.

During the last decade increasing attention has been devoted to kinetic and thermodynamic differentiation of Al species by flow-injection analysis, which has distinct advantages, e. g. high reproducibility and accurate reaction-time control, can be coupled with many used detectors. Its very great importance is a reduced human participation in time –consuming operation such as sample conditioning, reagent manipulation and calibration of measuring system (Pyrzynska et al., 2000)

4. Methods based on ion-exchange

Reactive Al species can be separated from less reactive species by using cation-exchange or chelating resins. This can be accomplished either by short-term batch reaction with a resin or by using column techniques. The batch technique determines reactive monomeric Al by difference in solution aluminium before and after reaction with the resin. This technique was applied for chemical partitioning of Al in soils contaminated by mining activity – Šobov, Slovakia (Matúš et al., 2003). The column techniques can be separated into two types. The earliest and most commonly used method was developed by Driscoll in 1984. With this method a small column of commercialy available, strong acid cation-exchange resin is used to remove reactive monomeric aluminium which is subsequent determined as a difference between Al concentrations in the influent sample and in the effluent solution.

5. Ion chromatographic separations

Ion chromatography with low capacity columns can be used directly to determine Al^{3+} plus hydroxy and sulphato monomers. Ion chromatography coupled with post column reaction with either tiron, pyrocatechol violet or 8-hydroxyquinoline-5-sulphonate, and fluorescence detection for very low Al concentrations and UV detection to higher ones is used (Willet, 1989). The ion-pair chromatography with a stationary phase of unpolar polystyrene-divinylbenzene resin and a mobile phase of lipophilic ions can be used to determination of Al complexes with fluoride and several organic ligands (Michalas et al., 1992).

Among the advantages of ion chromatography it is worth mentioning the very small sample volumes used, the speed of analysis and the possibility of making a direct measurements of individual monomeric forms of Al. It also be possible to determine some fluoride complexes separately, which is difficult with most other methods.

6. Methods based on ion mobility in an electric field

The differential mobility of ions in an electric field as a basis for separation has been used for many decades, primarily for the separation of macromolecules. The first to use it for fractionation of Al were Schmidt et al., 1989. They used isotachophoresis for separation and specific measurement of $[Al(H_2O)_6]^{3+}$ with conductometric detection. The capillary zone electrophoresis was used for separations of AlF^{2+} and AlF_2^+ from „free" Al from its oxalate complex (Wu et al., 1993)

Compared with other methods, electrochemical approaches are more sensitive, easy to perform, less time-consuming and require cheaper instrumentation but it can be realized by regulating the pH of the solutions investigated and using highly selective organic chelants targeting each Al fraction. The utilization of these properties for choice of optimum experimental conditions means that different laboratories in which different chelants have been used in adsorption complexing voltammetry for Al speciation in a variety of real samples give the reliable results (Bi et al., 2001)

7. ^{27}Al nuclear magnetic resonance (^{27}Al NMR)

Aluminium –27 is a nucleus with high intrinsic NMR sensitivity. Its natural abundance is 100% and it has a small quadrupole moment and a high resonance frequency. As a rapid, direct, and non-destructive analytical tool, Al NMR has been widely used to investigate the hydrolysis of Al in the presence and absence of organic and inorganic ligands, to study the structure and reactivity of Al^{3+} complexes with environmentally important ligands, and for quantitative determination of different Al^{3+} species present in environmental samples (Kot et al., 2000; Miyazaki et al., 1999).

The main disadvantage of ^{27}Al NMR in practical analysis is its limited sensitivity. Most studies have been conducted on total Al concentrations in the mmol L^{-1} range. These concentrations are far beyond the concentration range found in natural soils and aqueous systems (total $Al^{3+} \leq 10 \mu mol\ L^{-1}$).

8. Hybrid techniques

Coupled techniques have played an important role in Al speciaton analysis during the last five years (Kot et al., 2000). The combination of techniques of chromatographic separation, e. g. high-performance liquid chromatography (HPLC), or fast protein liquid chromatography (FPLC) coupled with a specific element detection technique such as ET AAS, ICP MS, ICP AES forms an extremely powerful analytical system for the direct speciation of Al. These techniques have several distinct advantages: very low detection limits for Al, rapid separation procedures, closed instrumental system effectively minimizes trace contamination and losses of analyte .

9. Computer simulation

Computer simulation models based on chemical equilibrium calculations are very useful tools for investigation of metal speciation in the environment. Development and application of a variety of computer models for predicting Al speciation in practice under different conditions have been reported, for example general implications of Al speciation-dependent kinetic dissolution rate law in water-rock modeling, speciation and solubility relationships of Al in solutions associated with sulphuric acid leached mine waste rock, etc. These have been essential in increasing our understanding of the interactions between hydrological and geochemical processes. Many models have been developed on the speciation of Al, for example MINEQL, GEOCHEM, WHAM, ALCHEMI, ALSCM (Bi et al., 2001)

Conclusion

The state of the art and the applicability of the different methodologies for quantitative determination of Al species are limited by three problems:

1. unsatisfactory detection limits for practical use in environmental samples,
2. operational definition of Al fractions causes problematic application to real samples and difficult comparisons among different laboratories,
3. absence of suitable certified reference materials which do not permit the procedures to be validated.

Hyphenated techniques (coupling of HPLC/ FPLC with ICP MS/ ETAAS/ ICP AES, etc.) are currently the primary tool for species-selective analysis of Al. Simplification, reduction in cost, and increasing the robustness of the techniques are , however, still necessary.

The advantages of ^{27}Al NMR are its speed, its response to different kinds of coexisting species, no alteration of the sample, and provision of both quantitative and structural information. The application of this method to natural samples is still scarce, because of its limited sensitivity.

On the basis of the thermodynamic and kinetic characteristics of complexing chelants reacting with Al, the toxic forms of Al and total monomeric Al can be satisfactorily determined by FIA and electrochemical analysis. The distinct advantage of these methods are higher sensitivity, high speed, no separation step, and cheaper instrumentation.

Al speciation by computer models plays an important role in evaluating Al species in environment and assessing its ecological risk.

Acknowledgement

This work was financially supported by the Scientific Grant Agency of Ministry of Education of Slovak Republic, grant No. 1/0031/03.

References

Beckett, P. H. T., 1989: The use of extractants in studies on trace metals in soils, sewage sludges, and sludge-treated soils. Advances in Soil Science, 9, 144-176.

Bi SP., Yang XD., Zhang FP., Wang XL. & Zou GW., 2001: Analytical methodologies for aluminium speciation in environmental and biological samples-a review. Fresenius J. Anal. Chem., 370, 984-996.

Clarke, N, Danielsson, L-G & Sparén, A., 1996: Analytical methodology for the determination of aluminium fractions in natural fresh waters. Pure & Appl. Chem., 68, 1597-1638.

Dlapa, P., Kubová, J., Matúš, P. & Streško, V., 2002: Chemical and physical aluminium speciation in soil solutions. Fresenius Environmental Bulletin, 11, 626-630.

Driscoll, C. T., 1984: A procedure for the fractionation of aqueous aluminium in diluted acidic waters. Int. J. Environ. Anal. Chem., 16, 267-273.

Kot, A. & Namiesnik, J., 2000: The role of speciation in analytical chemistry. Trends Anal. Chem., 19, 69-79.

Kubová, J., Matúš, P., Streško, V. & Bujdoš, M., 2003: Chemical partitioning of aluminium in soils contaminated by mining activity. CSI XXXIII Granada, Spain, Actas, 425.

Matúš, P., Kubová, J. & Streško, V., 2003: Utilization of chelating ion exchange for aluminium speciation. Chem. Pap., 57, 176-178.

Michalas, F., Glavac, V. & Parlar, H., 1992: The detection of aluminium complexes in forest soil solutions and beech xylem saps. Fresenius A. Anal. Chem., 343, 308-312.

Miyazaki Y., Hiramatsu E., Miura Y. & Sakashita H., 1999: ^{27}Al NMR studies on the complezation of aluminium(III) with phosphinate and phosphite ions. Polyhedron, 18, 2041-2045

Pyrzynska, K., Gucer, S. & Bulska, E., 2000: Flow-injection speciation of aluminium. Wat. Res., 34, 359-365.

Schmid, S., Kördel, W., Klöppel, H. & Klein, W., 1989: Differentiation of Al^{3+} and Al species in environmental samples by isotachophoresis. J. Chrom., 470, 289-297.

Sposito, G., 1996: The Environmental Chemistry of Aluminium. (ed. Sposito G.). CRC Press, Boca Raton, USA.

Sutherland, R. A. & Tack, F. M. G., 2002: Determination of Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedure. Anal. Chim. Acta, 454, 249-257.

Wilett, I. R., 1989: Direct determination of aluminium and its cationic fluoro-complexes by ion chromatography. Soil Sci. Soc. Am. J., 53, 1385-1391.

Wu, N., Horvath, W. J., Sun, P. & Hurie, C. W., 1993: Speciation of aluminium using capillary zone electrophoresis with indirect UV detection. J. Chromatogr., 635A, 307-312.

Slovak Geol. Mag., 9, 2– 3(2003), 129 – 131

Optimalization of Sequential Extraction Method for Determination of Toxic Elements in Soils and in Stream Sediments

DANIELA MACKOVÝCH, JARMILA NOVÁKOVÁ and HENRIETA ŠOLTÝSOVÁ

Geological Survey of Slovak Republic, Geoanalytical Laboratories, Spišská Nová Ves

Abstract. This study concerns the optimalization of sequential extraction method for the determination of Al, As, Cd, Cu, Cr, Hg, Pb and Sb in soils and stream sediments. These toxic elements were divided into five fractions: water soluble fraction, ion – exchange and carbonate fraction, reducible fraction, organic – sulphide fraction and residual fraction. Experimental results demonstrate that the precision of the determination was between 10 and 20 %. The quality was tested on a sediment reference material CRM 601. Experimental and certificated results show a good agreement. The time of extraction and tested stability of extraction solutions were optimalized for each step of sequential extraction. Sequential extraction procedure gives useful information about geochemical forms of trace toxic elements in stream sediments and soils.

Key words: sequential extraction, stream sediment, soil, toxic element

Introduction

Recently geochemical research has changed its aim from the monitoring of total concentrations of elements into studying of its forms in a given system. The total content of element in a sample is not an appropriate indicator of its biological availability. The toxicity of the element depends on its chemical form, mobility, transformation and biologically available for plants. Toxicologists´ knowledge of a different scale of toxic effects of compounds of heavy metals and metaloids on living organisms led to efforts to analytical resolution of different forms of elements´ bonds in the enviromental samples and in biological materials. The quantification of chemical forms of elements in soils and sediments forms the basis for monitoring of bioavailibility and mobility in the environment.

Method selection and its optimalization

The method of the sequential extraction was chosen on the basis of results to the recommendation of Community Bureau of Reference (BRC) according to the methodology of Fiedler, H. D. and all, (1994). This methodology was tested and accepted by several European laboratories. It is a three-step sequential analysis. Certified reference material, which was prepared through the international laboratory test, is used to check accuracy and precision of analyses.

Except for the suggested steps of extraction we also added first step for extractible elements in water phase and last fifth step for the determination of element content in the residual bonded on silicate minerals.

The scheme of sequential extraction used in this study classifies metals into the following fractions:

a) **water soluble fraction (1)** – characterises trace elements dissolluble in water phase in the form of mostly inorganic salts,

b) **ion – exchange and carbonate fraction (2)** – characterises trace elements adsorbed on anorganic salts and carbonates, which are released into water if neutral conditions change into slightly acid conditions,

c) **reducible fraction (3)** – characterises elements associated with oxides of Fe and Mn, which are thermodynamically unstable and they release trace elements into water with a change of redox potential,

d) **organic – sulphide fraction (4)** – characterises the fractions of elements bonded in organic substance and in sulphides. These elements are released into water as the result of oxidation and a sequential degradation of organic substances and a decomposition of sulphides by the change of physical and chemical conditions,

e) **residual fraction (5)** – determines a fraction of elements bonded on primary and secondary minerals, which do not commonly release into water surroundings in nature.

Extraction method

One gram of sample was used for the determination of extractible specific forms of elements - Al, As, Cd, Cu, Cr, Hg, Pb and Sb. The extraction was carried out in every step in a laboratory shaker during 16 hours, at 200 counts per one minute and at a temperature of 20 ± 2 °C. The sample was kept in suspension during the extraction. The extract was separated from the solid residue by centrifugation and decantation of the supernatant liquid into polyethylene container and stored at 4 °C prior to analysis. The optimalization of this method was performed on five stream sediments and five soil samples. According to the concentrations of determined elements upper mentioned samples were chosen.

The following analytical methods were used for the determination of the tested elements:

Al, Cr, Cu, Pb atomic emission spectrometry with inductively coupled plasma

Cd atomic absortion spectrometry with electrotermic atomization

As, Sb atomic absorption spectrometry with hydride generation

Hg atomic absorption spectrometry

The total mineralogical composition of soils and sediments was measured by X-ray difraction.

The total content of **Cr** in the sample was measured by the method of X – ray spectrometry (XRFS) on a spectrometer Spectro X – LAB 2000. The content of Cr was measured directly in extraction solutions (except in fraction 5). The content of Cr in fraction 5 was defined by subtracting from the total content of Cr in all four fractions measured by the method of XRFS.

Because of signal depression the method of calibration curve could not be used to measure **As** and **Sb** by hydride generation and **Al, Cr, Cu, Pb** by atomic emission spectrometry with inductively coupled plasma. The technique of spiked sample was used to determine and to eliminate interferences of matrix elements. Predetermined amounts of analyt were added into the sample solutions. The additions contained from 100% to 200% of the analyt in each sample. On the basis of experimental results of interferential influences during the determination of **As** and **Sb** in the environmental samples (Mackových, 1987), the influence of elements in solutions was monitored. Maximum acceptable concentrations of interferential elements are introduced in the table below.

The pilot samples of stream sediments and soils were used to test the technique of evaluation of an analytic signal by the method of a calibration curve or by the procedure of a standard addition. It was proved that extraction test solutions of the fractions did not have any influence on the intensity of the signal and on the effectiveness of a hydride generation. The results obtained by the method of a calibration curve and by the technique of a standard addition were identical. Therefore the method of a calibration curve was chosen for the evaluation of the signal.

Hg was measured by the method of AAS. The results of sequential extraction on standard samples show that the largest quantity of Hg was extracted in organic – sulphide fraction and that the residue left in the fraction 5. The oxidizing of Hg in organic – sulphide fraction (step 4) was performed by the influence of H_2O_2. By heating of the sample on approximately 85 °C Hg became a solution but with the loss of Hg in a form of vaporizable compounds. For this reason the content of Hg was extractible in the organic – sulphide fraction and it was determined in a solid residue after the extraction in step 4. The extractible amount of Hg in step 4 was determined by the formula introduced below:

$$c_{Hg(4)} = c_{Hg(T)} - c_{Hg(1)} - c_{Hg(2)} - c_{Hg(3)} - c_{Hg(5)}$$

$c_{Hg(T)}$ = total content of Hg

$c_{Hg(1)\,\ldots\ldots\,(5)}$ = content of Hg in the fractions 1 - 5

Extraction time optimalization

Extraction time was an important indicator for suggesting an optimal method of sequential extraction not only for analytical but also for economical aspects. Proposed extraction time was 16 hours. Extraction times of 6, 8 and 16 hours were chosen for this research. The experiments were done on two pilot stream sediments. After the extraction the solutions were separated and the trace elements were determined. The recovery of the extraction was evaluated on the basis of recovery. The value of analyt after sixteen – hour extraction in all steps was chosen as 100 % recovery. The recovery of extraction in second step for Cd was lowered. After six / eight hours about 70 % of Cd was extracted. The recovery of extraction was higher in step 3 of the value which had not extracted in step 2. For Cu the recovery of extraction was lower of 30 % in step 2 and lower of 10 % in step 3. Six – hour extraction was convenient for the other elements. On the basis of upper mentioned results 16 – hour extraction was used for all other experiments.

Precision

The precision was evaluated from the measured results of a monitoring sample 4Sp – 2364. This sample was analyzed 18 times. The precision of determination was calculated for each element in all five fractions. The results are introduced in table 2. The precision of determination is in a range of 10 –20 %. The values of RSD

Accuracy

Certified reference material of the stream sediment CRM 601 which was prepared by the Community Bureau of Reference was used for accuracy testing. This certified reference material was analyzed by 3 – step sequential extraction. The second, third and fourth steps of the extraction used in this study are identical with upper mentioned extraction.

Certified elements:	2nd step – Cd, Cr, Ni, Pb, Zn
	3rd step – Cd, Ni, Zn
	4th step – Cd, Ni, Pb

The recovery was evaluated for the following elements Cr, Cu, Pb and Cd whose content in reference material had been certificated. According to the results of the BCR comission of interlaboratory comparisons, the agreement among determined results is satisfactory if the difference of results is < 30 %, which was approached in all determinations except Cd. The content of Cd was determined 36 % higher in step 3 and 33 % lower in step 4. However it is not an important difference because of low contents of Cd. The results of determinations and recovery are introduced in table 3.

Analytical quality of elements determination in batch analyses was checked by a chosen monitoring sample – internal reference material which was analysed with every series of samples.

Stability testing of extraction solutions

The solutions obtained by 5 – step extraction were after the separation from solid residue kept in a refrigator at approximately 4 °C. The stability of solutions was tested during two months. The solutions were analyzed

Table 1: Maximum acceptable concentrations of interferential elements

Analyt	**Maximum concentration of interferent in a measured solution (µg/ml)**									
	Fe	Ca	Co	Ni	Cu	Pb	Zn	As	Bi	Sb
As	1000	5000	1.0	1.0	5.0	1.0	7.5	-	1.0	0.2
Sb	1000	5000	1.0	1.0	5.0	1.0	2.0	0.2	0.5	-

Table 2: Precision of determination of elements in fractions 1 - 5

Fraction	Cu			Pb			Cr			As		
	Average	SD	RSD	Average	SD	RSD	Average	SD	RSD	Average	SD	RSD
	µg/g	µg/g	%	µg/g	µg/g	%	µg/g	µg/g	%	µg/g	µg/g	%
1	5	0.7	14	<2			<1			1.4	0.5	36
2	37	1.7	5	4	0.4	10	<1			<0.1		
3	137	11.7	9	85	6.4	8	4	0.5	13	22	2.4	11
4	120	7.9	7	8	1.9	21	6	0.9	15	4.8	1	21
5	46	3.4	7	13	1.8	14	101	5.5	5	50	3.1	6
Σ	344			111						78.2		
TOTAL	376			116			111			77		

Fraction	Sb			Cd			Hg			Al		
	Average	SD	RSD	Average	SD	RSD	Average	SD	RSD	Average	SD	RSD
	µg/g	µg/g	%	µg/g	µg/g	%	µg/g	µg/g	%	µg/g	µg/g	%
1	1.5	0.3	20	<0.01			0.003	0.002	67	21	6	29
2	0.5	0.2	40	1.63	0.44	27	0.009	0.002	22	82	12	15
3	1.5	0.2	13	0.38	0.12	32	0.011	0.002	18	1131	155	14
4	0.5	0.07	14	0.11	0.03	27	5.73	0.15	3	468	42	9
5	41.5	2.2	5	<0.5			2.12	0.13	6	56850	850	1
Σ	45.7			2.11						58552		
TOTAL	46			2			7.86			62600		

Table 3: Comparison of measured and certified values for elements in CRM 601

Frac-tion	**Cr**			**Cu**			**Pb**			**Cd**		
	A [mg/g]	B [mg/g]	R [%]	A [mg/g]	B [mg/g]	R [%]	A [mg/g]	B [mg/g]	R [%]	A [mg/g]	B [mg/g]	R [%]
2	<1	0.39	98	7.6	8.3	92	<2	2.28		4.1	4.14	99
3	10.4	10.6	86	71	72.8	98	199	205	97	4.2	3.08	136
4	17.3	20.1		93	78.6	118	25	19.7	127	1.4	1.83	77
5	128			64			37					
Σ	156			235.6			261			9.7		
Total	151	148	102	246			264	231	114	12.4		

A-measured value B-certified value R-recovery

straight after extraction, after one week, after one month and finally after two months. Any change of the concentrations of solutions were not observed during the whole period of our testing. The solutions are stable for at least 2 months if they are stored at temperature of 4 °C.

Conclusion

The aim of this study was to test the new analytical methodology of determination of chosen toxic elements by 5 – step sequential extraction. The methodology of extraction was chosen on the basis of the recommendations of Community Bureau of Reference BCR. Sequential extraction does not only have analytical importance – it offers ability to compare results among laboratories and the use of reference materials, but the main reason of its importance is in comparing levels of contamination of different areas.

The optimalization of analytic method was done on pilot samples of stream sediments and soils. Our attention was directed to the method of extraction, time stability of extracted solutions, precision, accuracy, recovery, frequency testing and long – term stability of analytical process.

On the basis of experimental results it can be stated that 5 – step sequential extraction is suitable for study of batch analyses of distribution of chosen toxic elements in stream sediments and in soils.

References

Fiedler, H.D., Lopez-Sanchez, J.F., Rubio, R., Rauret, G., Quevauviller, P., Ure, A.M.&Muntau, H., 1994: Study of the stability of extractable trace metal contents in a river sediment using sequential extraction. Analyst, 119, 1109-1114.

Mackových, D.: Aplikácia hydridovej techniky pri analýze geologických materiálov, Kandidátska dizertačná práca, Košice 1994.

Slovak Geol. Mag., 9, 2 – 3 (2003), 133 – 136

Determination of Removable Portion of Some Elements in Stream Sediments of Spišsko-gemerské rudohorie Mountains*

[1]VOJTEKOVÁ, V., [2]KRAKOVSKÁ, E., [3]MACKOVÝCH, D., [3]NOVÁKOVÁ, J. and [3]ŠOLTÝSOVÁ, H.

[1]Department of Physical and Analytical Chemistry, Institute of Chemical Science, University of P. J. Šafárik,
Šrobárova 2, SK- 041 80 Košice, Slovakia, e-mail: vojtekv@kosice.upjs.sk
[2]Department of Chemistry, Faculty of Metallurgy, Technical University, SK-042 00 Košice, Slovakia
[3]Geol. Survey of Slovak republik, Geoanalytical Laboratories of Spišská Nová Ves, SK-052 04 Spišská Nová Ves, Slovakia

*Abstrakt.*The single extraction with 0,05 mol dm^{-3} EDTA recommended for leaching of soils was modified for this study. Information capacity (removal ability) of this single extraction was compared with operationally used sequential extraction procedure. Single and sequential extraction procedures were applied on four sediment samples coming from industrially polluted region of the Eastern Slovakia. This paper describes the preparation of samples, gives analytical results in each extraction step for Cd, Pb, Cu, Cr and Ni and brings comparison of these results with total element content analyses realized by independent spectral method.

Key words: fractionation analysis, sediments, environmental protection, single-step extraction, sequential extraction, AAS, ICP OES, XRF

Introduction

Actual geochemical research has skipped from total element contents observation to the study of elements forms in chosen systems of environment /water, soils, sediments/. Information about different degree of toxic effects of several element compounds on biological systems, gave birth to the effort of analytical resolution – fractionation of several element-binding forms in environmental and biological materials (Templeton, 2000).

The observation of chemical composition of stream sediments and phase distribution of element binding forms is useful in geological prospecting and environmental protection. Their influence on the environment is not limited on the stream bed. Quantification of chemical and binding forms of elements in sediments has given the basis for monitoring of bioavailability and mobility of contaminants in environment (Batley,1990). In comparison with a water analysis, "stream sediment samples" are more suited for a geochemical and environmental evaluation thanks to their good accumulative properties.

Fractionation analysis using sequential extraction like a method brings comprehensive information about potential mobility of metal contaminants but it is time consuming. Application of uniformed sequential extraction advances is necessary because of significance and comparability of extraction results.

In this work normative "soil extractioń procedure" into 0,05 mol dm^{-3} EDTA (Ure,1995) for sediments was modified and compared with the results of operationally used sequential extraction procedure. Applied sequential extraction is a modification of BCR (Community Bureau of Reference) recommended extraction (Mackových et al., 2000) In this paper the results of this comparison is presented. The sediment samples from industrially stressed area of Spišsko-Gemerské rudohorie Mountains were studied and spectral methods like element detection are used.

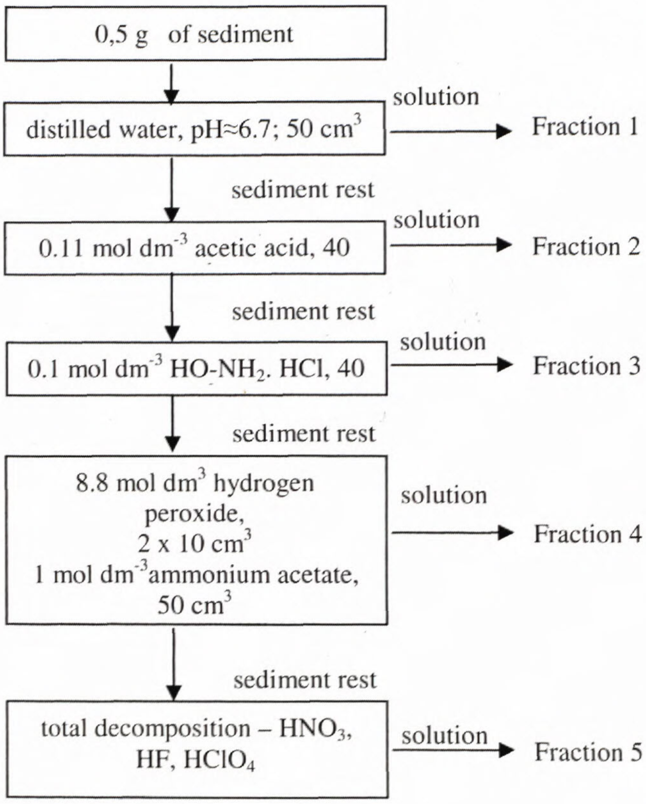
Theoretical

The natural sediment is a full mixture of several phases, especially of weathering and erosion rests of clay materials, aluminosilicates, iron and manganese hydroxides, sulphides, carbonates, and particles coming from biological and industrial activities, which are transported through liquid phase. River sediment is a complicated dynamical system, which is chemically and biologically reactive. Time of element abidance in existing form is different, depends on element character, on physicochemical form, kind of chemical binding, mobility, and external conditions of systems. Precipitation and adsorption of metals from aquatic phase on sediment surface are seldom controlled by the formation of well-defined poorly soluble complexes (Hakansson, 1989).

For fractionation study of soils, sediments, and sludge many selective extractive advances were developed, which consist in consecutive-sequential leaching of element portion bound on main components of solid sediment phase. The most frequently used leaching advance was the method developed by *Tessier* (Tessier, 1988). It was applied and seriously tested by a great number of authors and the above-mentioned "BCR extraction" is a modification of Tessier scheme too (Fiedler et al., 1994). It deals with three-step sequential extraction.

In modified and here used extraction procedure except of the proposed extraction steps the first step for elements extractable at water phase and the fifth step for determination of element contents in sediment rest were added. Detailed description of distribution of sediment fractions, formed during applied five-step extraction is listed in Reference (Vojteková et al., 2002) and final sequential extraction scheme is listed in Fig. 1.

Fig. 1. Description of the applied sequential extraction scheme (Mackových et al., 2000).



Experimental

The fluvial sediment samples were taken in industrially stressed region Spišsko-Gemerské Rudohorie Mountains (Method. Instr.), four sampling places were chosen /Table 1/. Samples were dried at temperatures to 40 °C, then sieved and milled in agate planetary treadmill on fineness under 0.09 mm. For assessment of extractable element share of Cd, Cu, Cr, Pb and Ni 0,5 g of homogenized sample was weighted.

The original protocol for 0,05 mol dm^{-3} EDTA extraction of soils for sediments of chosen region was optimised. During optimisation were changed some conditions listed in table 2. Extraction ratio 1:50 means 0,5g of sample: 25 cm^3 of 0,05 mol dm^{-3} Na_2EDTA; 1:100 means 0,5g of sample: 50 cm^3 of 0,05 mol dm^{-3} Na_2EDTA and 1:150 means 0,5g of sample: 75 cm^3 of 0,05 mol dm^{-3} Na_2EDTA. Optimisation is shown for most contaminated sediment 3.

Sequential extraction (detailed conditions in Fig 1.) In each individual step was performed in a mechanical shaker for 16 h (number of vibrations 200 min^{-1}, temperature (20±2) °C). After finishing the extraction the solution was centrifuged by 4000 rpm, for 20 min. Solutions obtained from individual extraction steps were saved in polyethylene vessels at temperature 4 °C. From the solution prepared in the described way, extractable shares of chosen elements were determined and results are average values of 5 repeated analyses.

Table 1. Sampling Places of Chosen Region

Description of sample	Place of sampling	River / Stream
River Sediment 1	Rudňany - Markušovce	Hornád
River Sediment 2	Slovinky	Poráčsky jarok
River Sediment 3	Richnava	Hornád
River Sediment 4	Jaklovce	Hnilec

For determination of studied elements in each leached fraction the following analytical methods were applied: for Cr, Cu, Pb and Ni – atomic emission spectrometry with inductively coupled plasma and ultrasonic nebulization of sample, for Cd – atomic absorption spectrometry with electrothermal atomization. AES measurements were carried out by spectrometer Liberty 200 (Varian) with ultrasonic nebulizer (Cetac) and AAS measurements by atomic absorption spectrometer Spectr AA-400 with electrothermal atomizer GTA-96 (Varian). For the determinations of total element contents in studied sediments roentgen-fluorescent spectrometry has been applied and measurements were realized by spectrometer Spectro X-LAB 2000.

Results and discussion

Optimisation of single-step "EDTA extraction" is possible to discuss as follows:

As shown in Fig. 2, 3, 4,5 and 6 the optimised extraction ratio for each sediment is 1:150 , optimised time of single extraction is 6 hours and the highest recoveries are observed in extraction medium with pH = 3, but pH =3 is not probable in real conditions of water-sediment system. There is more interesting optimise pH of "EDTA extraction" according to acidity of top water.

On the strength of comparison single and operationally used sequential extraction procedure about the removal ability of Na_2 EDTA is possible to state: Extraction into Na_2EDTA is after optimisation in good accordance with sum of 1st, 2nd, 3rd and 4th step of sequential extraction procedure. From the sediment matrix of chosen sampling areas with 0.05 mol dm^{-3} Na_2EDTA it is possible to extract shares corresponding to the first three /Fig. 7--10 for Ni, Cd, Pb, Cr, / or first four steps /Fig. 11 for Cu/ of sequential extraction. Into Na_2EDTA extracted contents and sum of contents extracted during 1st 2nd and 3rd step of sequential extraction procedure are practically identical for Cd, Pb, Cr and Ni and higher for Cu. Extraction efficiency is (for chosen sediment samples) element-specific and dependent on the composition of sediment matrix.

Conclusions

Single-step leaching advance into Na2EDTA, or the other chelating agent, is able /after optimisation of extraction conditions according to regional geological particularities/ to release mobile and mobilizable metal forms

Tab. 2. Standard and modified procedure for single extraction of into 0,05 mol dm^{-3} EDTA-salt for the elements Cd, Pb, Cu, Cr, Ni and Zn

Standard procedure		Optimisation of standard procedure
extraction agent	$(NH_4)EDTA$	Na_2EDTA
time of extraction	1 hour	1-6 hours, without pH modification, pH=4,7 1 hour during optimisation of pH
temperature	20±2 °C	20±2 °C
extraction ratio	1:10	1:50, 1:100, 1:150
acidity of extraction agent	pH=7(modified with NH_4OH)	pH = 3 -7 (1 hour- extraction during optimisation of pH, modified with HCl, NH_4OH)
Extraction wessel	250 ml PE (washed by H_2O 4M HNO_3 and 0,05M EDTA-salt)	
Filtration	„paper with blue stripe“ Θ = 18,5 cm	

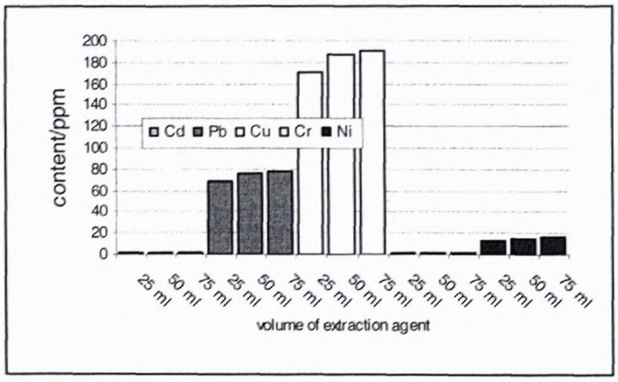


Fig 2. Optimisation of extraction ratio of studied elements- leaching agent 0,05 mol dm^3 Na_2EDTA

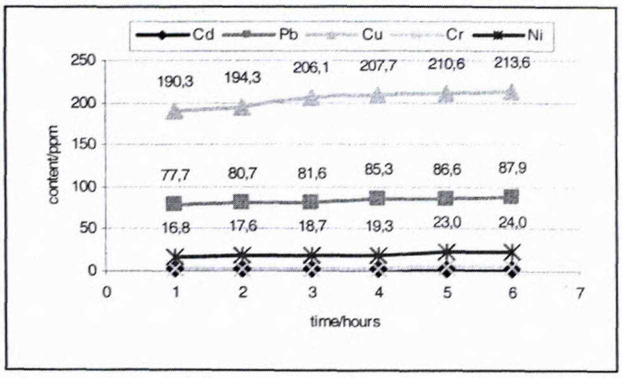


Fig 3. Optimisation of extraction time of studied elements, sediment 3- leaching agent 0,05 mol dm^3 Na_2EDTA without pH modification (pH of dilluted Na_2EDTA = 4,7)

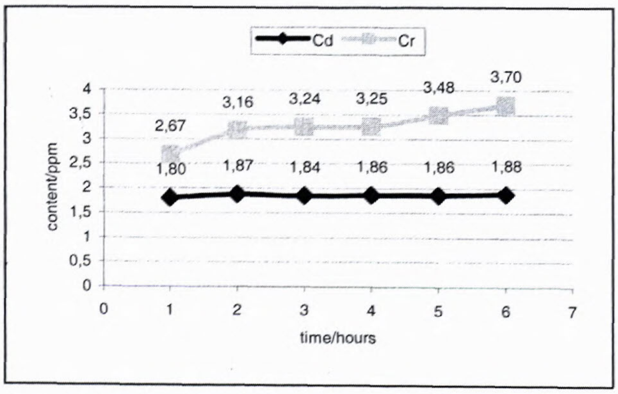


Fig 4. Optimisation of extraction time of studied elements, sediment 3,detail - leaching agent 0,05 mol dm^3 Na_2EDTA without pH modification (pH of dilluted Na_2EDTA = 4,7)

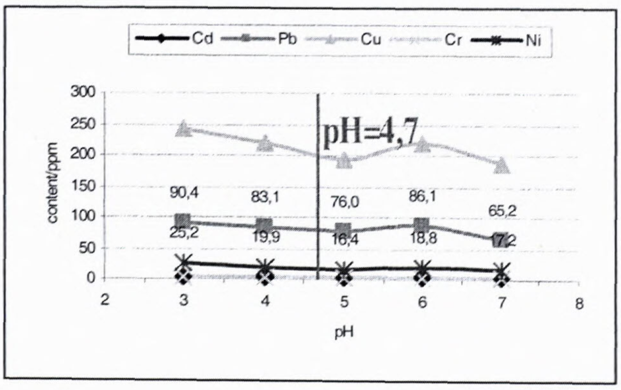


Fig 5. Extraction into 0,05 mol dm^{-3} Na_2EDTA, sediment 3 – optimisation of pH, pH = 4,7 – acidity of 0,05 mol dm^{-3} Na_2EDTA without modif

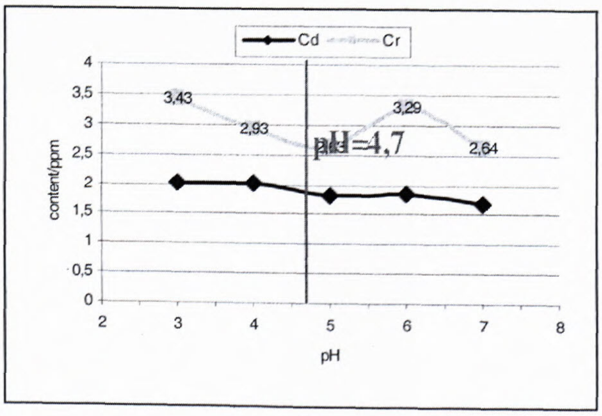


Fig 6. Extraction into 0,05 mol dm^{-3} Na_2EDTA, sediment 3, detail – optimisation of pH, pH = 4,7 – acidity of 0,05 mol dm^{-3} Na_2EDTA without modification

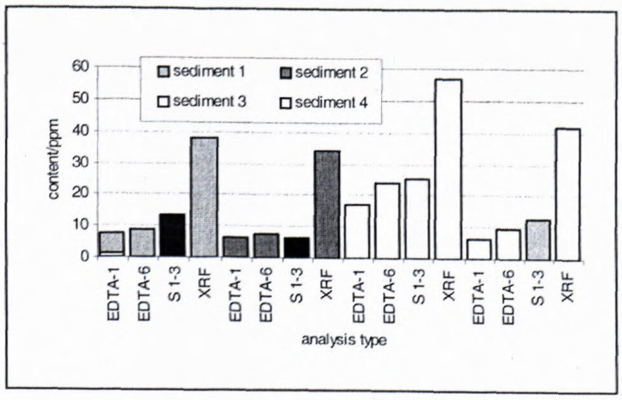


Fig 7. Comparison of Ni extracted shares during single and sequential extraction with total content analysis

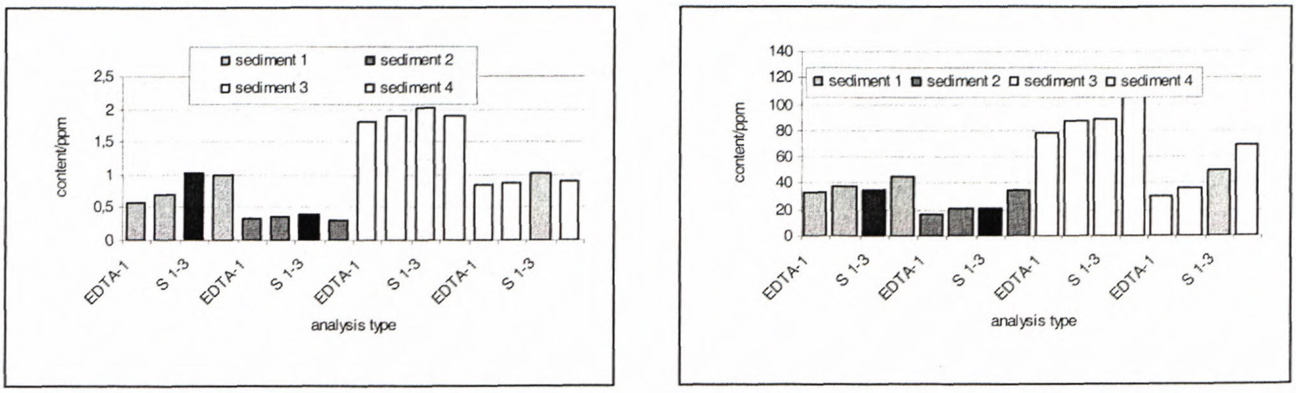


Fig 8,9. Comparison of Cd and Pb extracted shares during single and sequential extraction with total content analysis

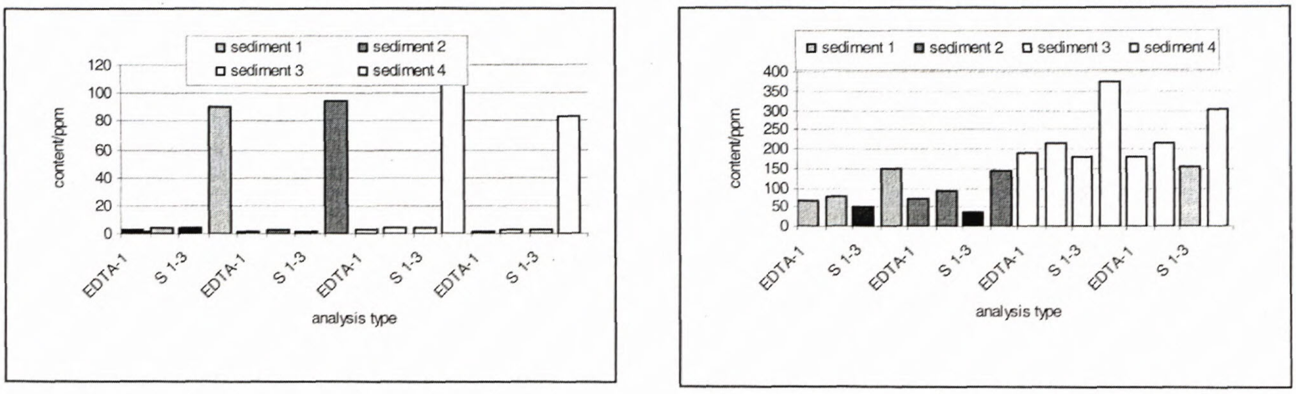


Fig 10, 11. Comparison of extracted shares of Cr and Cu during single and sequential extraction with total content analysis
Notice: EDTA - 1 -- extraction into 0,05M Na_2EDTA without modification of pH; pH= 4,7, time of extraction 1 hour, EDTA - 6 -- extraction into 0,05M Na_2EDTA without modification of pH; pH= 4,7, time of extraction 6 hour, S 1-3 -- sum of the first, second and third step of the five-step sequential extraction procedure, XRF -- total content analysis - control of accuracy of sequential extraction procedure by independent analytical method (XRF

retained in different modes and associated with specific sediment fractions.

Because of them "Na_2EDTA extraction" could be a form of the screening control of the sediments pollution /in local tested conditions - e.g. polluted regions of Slovakia/ and could be used like economically interesting and time saving supplementary test to recommended attested BCR sequential extraction procedures and fast alarm indication of element mobility changes in sedimentary systems.

Acknowledgements.

This work is a part of the Grant Project VEGA No. 1/0124/03 and 1/0386/03.The authors would like to express their gratitude to the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences for financial support.

References

Batley G.E., *Trace Element Speciation: Analytical Methods and Problems*. CRC Press, Inc., Boca Raton , Florida, USA, 1990.

Fiedler, H. D., Lopez-Sanchez, J. F., Rubio, R., Rauret, G., Quevauviller, P., Ure, A. M., and Muntau, H., *Analyst 119*, 1109 (1994).

Hakansson, K., Karlson, S., and Allard, B., *Sci. Tot. Environ. 43*, 87 (1989).

Mackových et al.: *Method of determination of chosen toxic element binding forms*, Subproject 2, GAL/ŠVL/ČS/3-2000, Geological Survey of Slovak Republic (2000)

Methodical Instruction of the Slovak Republic Ministry of Environment from 27th August 1998 No. 549/1998-2, for risk evaluations of contaminated fluvial and bed-load sediments.

Templeton, D. M., Ariese, F., Cornelis, R., Danielsson, L.-G., Muntau, H., Van Leuwen, H.P., and Lobinski, R., *Pure Appl. Chem. 72*, 1453 (2000).

Tessier, A. and Campbell, P. G. C., *Anal. Chem. 60*, 1475 (1988).

Ure A.M., Davidson C.M., Thomas R. P., *Quality Assurance for Environmental Analysis*. Elsevier Science, Amsterdam, Netherlands,1995.

Vojteková, V., Mackových, D., Krakovská, E., Remeteiová, D., and Tomko J, *Chem. Pap. 57 (3), 179* (2002).

Slovak Geol. Mag., 9, 2 – 3(2003), 137 – 140

Determination of Arsenic in the Process of its Drinking Water Removal

DANIELA BOROŠOVÁ[1], KATARÍNA VARGICOVÁ[2], ANTON AUXT[2]

[1]Štátny zdravotný ústav, Cesta k nemocnici 1, Banská Bystrica, borosova@szubb.sk
[2]HES-COMGEO spol. s r.o, Hlboká 16, Banská Bystrica, hes@penet.sk

Abstract. Inorganic arsenic is a multi-site human carcinogen getting into the body by drinking water route. The technology of As adsorption onto iron oxyhydroxide granules in the fluid bed reactor was applied to efficient arsenic removal from polluted drinking water below to accepted Slovak Standard. The technology was used in the middle Slovakia region. The As concentration decreased in Jasenie from value 0.041mg/L (0.033-0.048mg/L) and in Pohronský Bukovec from value 0.089mg/L (0.062-0.104mg/L) respectively, both to value less then limit of determination (<0.006 mg/L-ETA AAS method, <0.0016 mg/L-FI HG AAS method).

The addition of 5 – 6mg/L $FeSO_4.7H_2O$ is adequate for As removal at the level of pH in the water 6.5-6.7. A liquid retention time by 15 minutes is needed for the process. The consumption of O_2 during the reaction is approximately 2mg/L. The concentration of Fe does not exceed value 0.2mg/L (according to the Decree 29/2002 by the Ministry of Health) by treatment of water if all technological rules are kept.

The concentration of observed arsenic was measured by AAS method. The accuracy of analytical data was continuously secured by the system of analytical quality assurance and the principles of good laboratory practice.

The other water quality parameters in the treated water correspond to the requirements according to the Slovak Standard for drinking water.

The waste product is a compact iron granulate with high density (approx. 3kg/L) and a low water content (approx.10-20%).

Key words: arsenic, removal, fluid bed reactor, AAS

Introduction

Arsenic is an element that occurs naturally in rocks, soil, water, air, plants, and animals. There are numerous natural sources as well as human activities that may bring arsenic into drinking water. Inorganic arsenic can exert toxic effects after acute (short-term) or chronic (long-term) exposure. The World Health Organisation guidelines the amount of arsenic in drinking water to 10 μg/l as the maximum contaminant level (MCL). The limit was based on the re-evaluation of the uncertainties in arsenic risk assessment due to recent epidemiological evidence when the risk of cancer is considered (Okoji et al., 1999).

The MCL for arsenic in drinking water was defined in a Slovak Standard STN 75 7111 mandatory in the Slovak Republic (July 1998) and next in the Decree by the Ministry of Health 29/2002 about drinking water requirements and quality control (9th January 2002), as 0.01 mg/L.

The arsenic distribution in Slovak groundwater shows that higher concentrations of this element occur rarely most analyses was below the detection limit of the analytical method (1 μg/l), (Rapant et al., 1996). Higher contents have two sources: 1 sulphide deposits (Malé Karpaty, Nízke Tatry and Slovenské Rudohorie Mts.) and 2. Human-caused contamination sporadically distributed throughout Slovak territory, sometimes reaching concentrations of 50-250 μg/L (Šikulová, 2001).

Arsenic removal

The choice of a suitable treatment option for a specific water supply will depend on a number of factors, including the mandated arsenic concentration limit, the existing treatment system and the extent to which it can be modified to optimise arsenic removal, and other water quality parameters that must be met along with the arsenic standard. Different methods for arsenic removal are known, such as nanofiltration, reverse osmosis and flocculation/precipitation.

Materials and method

Chemical composition of groundwater reflects the underlying geology of the region. The groundwater in the Low Tatras infiltrates through granite and a Mesozoic belt, accumulates and rises from the huge layers of limestone-dolomite complexes. It spends a significant time in contact with subsurface rock and this results in the dissolution of minerals. The arsenopyrite FeAsS is the accompanying mineral in the wide range of rocks owing to increase the arsenic distribution in groundwater of the study region (Rapant et al., 1996). Therefore the higher concentration of As in drinking water is undesirable and has to be removed. Long-term values of arsenic concentration in the study region are given in the Table 1.

Table 1. Long-term values of arsenic concentration in the study region

Source	**Supplied village (Number of inhabitants)**	**Spring discharge (L/s)**	**As concentration (mg/L)**
Rastová	Jasenie, Predajná, Nemecká, (approx. 5000)	36.0	0.040-0.050
Sečе 1-4	Pohronský Bukovec, (approx. 100)	0.5-1.0	0.070-0.120
Vyvieračka	Brusno, (approx. 2000)	5.0	0.050-0.060
Kráľ Matyáš	Lopej, Podbrezová, (approx. 5000)	30.0	0.012-0.020

Chemical principles of applied technology (Nielsen, Christensen)

The treatment process operates by continuous addition of ferrous ions and an oxidation agent (O_2, H_2O_2, Cl_2) to the polluted raw water. Addition and mixing take place in a fluid bed reactor containing a carrier material. By controlling the process conditions, the oxidation of ferrous ions will take place heterogeneously after they have been adsorbed to the carrier material. An adsorptive granulate of oxyhydroxide will then be generated as a coating reddish-brown layer on the surface of the carrier material. Hence, the adsorptive surface is renewed permanently and the added iron is removed. Iron oxyhydroxide has significant adsorptive properties towards inorganic micopollutants, which are easily adsorbed onto surface of the carrier material. At the pH<7.8 it is capable to adsorb the ions and therefore to create the surface complexes, as follows:

$$FeOOH + HAsO_4^{2-} \rightarrow FeO(HAsO_4)^- + OH^-$$

$$-FeOOH(s) + Fe^{2+} + 1/4O_2 + 2OH^- \rightarrow -FeOOH-FeOOH(s) + \tfrac{1}{2}H_2O$$

In comparison to conventional chemical treatment with sludge production, no wash water is necessary; no sludge is created, waste product has the superb handling properties; the density of granulate is approx. 3kg/L. The waste stream is reduced; the water content is 10-20%. The operating and personnel ability costs are minimal.

Description of fluid reactor

The main part of equipment is the fluid reactor. It is a cylinder made of polypropylene, in dimensions according to the treated water output. It is filled with the quartz sand. The scheme of reactor is given in the Figure 1. The reactor is divided into four parts:

In *inflow part,* water is pumped through a jet system located at the bottom of the reactor. Water is divided to flow permanently with controlled speed. It provides the creation of sand fluid bed. Two jets add the chemicals.

Reaction part is filled by fine quartz sand. The sorption of formatted complexes is done on the surface of carrier material covered by iron oxyhydroxide.

The greater diameter of *calming part,* according to the reaction part, slows down the speed of flowing water and the separation of turbulating sand covered with the absorbing layer from the treated water occurs.

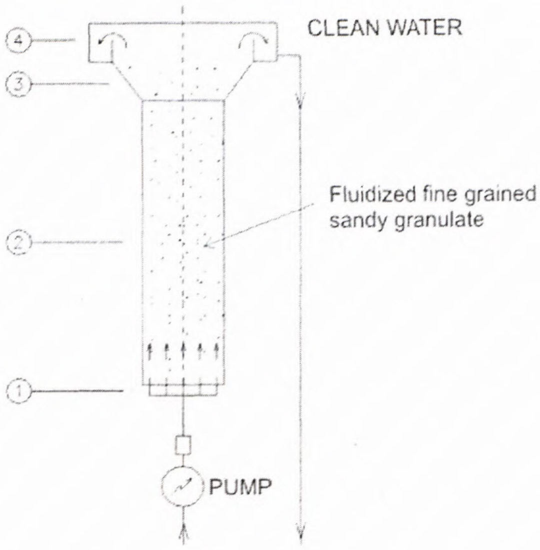


Figure 1. Scheme of fluid reactor: 1 - inflow part, 2 - reaction part, 3 - calming part, 4 - outflow part.

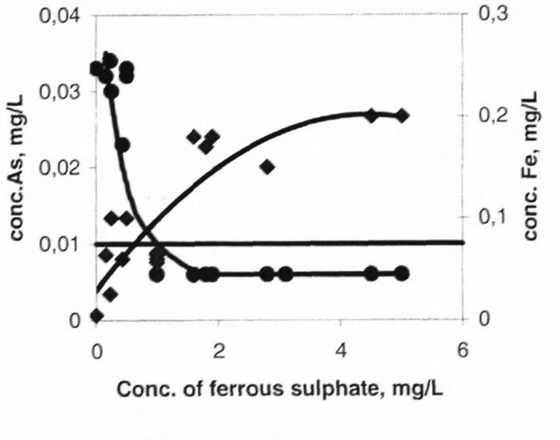


Figure 2. The observed As and Fe concentration in the treated water as a function of added $FeSO_4.7H_2O$

In *outflow part,* the treated water flows out gravitationally from the top of the reactor into accumulating tank and the sand returns back to the reaction part.

Test result

The recommended technology was applied in groundwater sources Jasenie and Pohronský Bukovec. Operating parameters: amount of $FeSO_4.7H_2O$ added, the volume of treated water and aeration was investigated. The observed As and Fe concentration in the treated water as a function of added $FeSO_4.7H_2O$ is given in Figure 2.

Table 2. Review of the analytical quality assurance

Test sample	Certified value µg/L	Observed value µg/L	Number, *n*	Method used
MT-ŠAA-5/2000[a]	14.0±2.1[b]	14.50±0.44	24	FI-HG-AAS
MT-SAA-9/2001[a]	9.90±1.98[b]	10.32±0.26	3	FI-HG-AAS
SRM 1643d	56.02±0.73	55.96±1.20	10	ETA AAS

a) Internal standard materials - samples obtained from the Slovak Water Management in the inter-laboratory test

b) values are based on the inter-laboratory tests

Table 3. Results of inter-laboratory tests

Test samples	Certified value µg/L	Accepted value µg/L	Observed value µg/L	*z*-score
MT-ŠAA-5/2000[a]	14	11.9-16.1	13.7	<-2, +2>
MPS-ŠAA-9/2002[a]	8	6.40-9.60	7.72	<-2, +2>
IMEP 12[b]	9.07	8.17-9.96	10.53±1.67	

a) The inter-laboratory tests of Slovak Water Management

b) The International Measurement Evaluation Programme (IMEP) was organised by the Institute for Reference Material and Measurements (IRMM), Geel, Belgium

Table 4. Spiked samples recovery

Test sample	As, added µg/L	Recovery %	Number, *n*	Method used
Randomly selected sample	10	101,0±6,3	16	FI-HG-AAS
	10	108,6±4,4	18	ETA AAS

The As concentration decreased in Jasenie from value 0.041mg/L (0.033-0.048 mg/L) and in Pohronský Bukovec from value 0.089mg/L (0.062-0.104 mg/L) respectively, both to value less then limit of determination (<0.006mg/L-ETA AAS method, <0.0016 mg/L-FI HG AAS method).

The optimal amount of added iron depends on the original concentration of As in the water, the temperature of the water, the amount of O$_2$, the time of the reaction and the amount of water to be treated. For monitored sources the addition 5 – 6mg/L FeSO$_4$.7H$_2$O is adequate for removal of As and it also decreases the level of pH in the water to the acceptable norm 6.5-6.7. The greater amount of Fe does not cause an increased effectiveness of the treatment, but it decreases pH under the level of 6.5. What is more, the concentration of Fe in outflow water is increased, what is undesirable. The interruption of dosing FeSO$_4$ and the interruption of aeration causes the suspension of the technology, it follows that the activated sand is not able to catch As.

The concentration of Fe does not exceed value 0.2mg/L (according to the Decree 29/2002 by the Ministry of Health) by treatment of water if all technological rules are kept. A liquid retention time by 15 minutes is needed for the process.

Water, that will be used, needs to be oxidised. The lowest necessary concentration of O$_2$ is 5mg/L. The shortage of O$_2$ does not influence removal of As, but it decreases the ability of creating and catching iron oxyhydroxide, that causes the increasing concentration of iron at the output of the reactor. The consumption of O$_2$ during the reaction is approximately 2mg/L.

The monitored parameters (pH, the amount of O$_2$, conductivity, temperature of water) in the treated water correspond to the requirements according to the Slovak Standard for drinking water.

Determination of As by AAS method

The arsenic concentration was measured by AAS method for the whole period. The Perkin-Elmer 4100ZL atomic absorption spectrometer with the Zeeman background correction, THGA furnace and the pyrolytic graphite platform tubes with end caps were used to all measurements. The lamp current 350 mA and the resonance line of 193,7 nm of arsenic electrodeless discharge lamp was set. The addition of 5µL Pd/Mg matrix modifier to 20µL sample aliquots was applied to avoid losses of arsenic during the ashing stage. The optimal furnace conditions - ashing temperature 1300°C and atomisation temperature 2200°C were found.

Nevertheless, the limit of determination (0.006mg/L) is not sufficient with respect to the 10% of MCL criteria for limit of detection defined in Decree 29/2002 by the Ministry of Health.

Therefore, a flow injection hydride generation AAS method was used to achieve high sensitivity and more reduction of matrix interference in the drinking water (LOD, 0.0005mg/L). Volatile arsine was generated in flow injection system FIAS 100 and transported to a quartz cell heated to 900°C, where the arsine was converted to gaseous metal atoms and then absorb the light from the EDL As lamp.

Arsine is more easily formed from As^{3+}. Samples to be analysed for As should be prereduced by the KI and ascorbic acid prior to analysis.

The accuracy of analytical data was continuously assured by the system of analytical quality assurance and the principles of good laboratory practice. The checks of analytical quality assurance comprised inter-laboratory analyses of water samples, spiked samples (matrix spike – standard addition of 10µg/L As is spiked to the randomly selected sample in the batch of samples), certified reference materials, parallel samples. The review of the items accomplished within analytical measurements is given in Tables 2-4.

Conclusion

Presented results show efficient applying of arsenic removal from polluted drinking water below to accepted Slovak Standard value by adsorption onto iron oxyhydroxide granules in the middle Slovakia region. The technology was operated in the fluid bed reactor. The concentration of observed arsenic was measured by AAS method. The other water quality parameters in the treated water correspond to the requirements according to the Slovak Standard for drinking water. The waste product is a compact iron granulate with high density (approx. 3kg/L) and a low water content (approx.10-20%).

References

Okoji,R.S., Leininger,J., Froines,J.R.: Subchronic Toxicity study of Sodium Arsenite in Methyl-Deficient Male C57BL/6 Mice. In: *Arsenic Exposure and Health Effects*, Elsevier Science B.V., 1999.

Šikulová, Z.: Arsenic, In: Virtanen, T.: *Water Chemistry*, Matej Bel University, Banská Bystrica, ISBN 80-88784-23-9, 2001.

Slovak Standard STN 75 7111, *Water Quality, Drinking water*. Bratislava : SÚTN, 1998.

Decree 29/2002 by the Ministry of Health about drinking water requirements and quality control, 9th January 2002.

Nielsen, P.B., Christensen, T. C.: Continues High-rate Removal of Nickel and Arsenic in a Fluid Bed Reactor, Krüger A/S, Denmark.

Christensen, T. C., Nielsen, P.B.: New Technology for Removal oh Heavy Metals from water, Krüger A/S, Denmark.

Slovak Geol. Mag., 9, 2– 3(2003), 141 – 144

Utilization of the Soil Magnetometry for Environmental Geochemistry of Heavy Metals

ONDREJ ĎURŽA

Department of Geochemistry Faculty of Natural Sciences Comenius University, Mlynská dolina,
842 15 Bratislava, Slovak Republic, e-mail: durza@fns.uniba.sk

Abstract. The origin of magnetic particles in the soil and a non-conventional way of utilizing magnetic susceptibility - soil magnetometry - was studied in Malé Karpaty Mts. (West Slovakia). Magnetic susceptibility values above background in soil samples indicate higher concentrations of heavy metals in soil, i. e. the soil magnetometry can be used as a preliminary quick and inexpensive method for detection of higher heavy metal contents in soils.

Keywords. Heavy metals, soil magnetometry, Malé Karpaty Mts.

Introduction

Heavy metals are important in several ways: many are used industrially in technologically advanced countries, some are physiologically essential for plants and animals - and thus have a direct bearing on human health and agricultural productivity - and many are significant as pollutants in ecosystems throughout the world.

Heavy metals in soils have received increasing attention in recent years (Chan at al., 1998; Dlapa et al. 2000; Kapička at al., 2000; Magiera and Strzyszcz, 2000). There were recommended by Mikľajev and Žogolev (1990) to use soil magnetometry like a preliminary method that enable to border zones „increased geochemical activity", to bring down a bulk of works and to change flexibly the method of mapping but also in study of surface sediments (Brandau and Urbat, 2000; Milička et al., 2002) and pedological study of paleosols and loess (Verosub et al., 1993; Cocuaud at al., 1998).

Detection of enhanced heavy metals levels in soil using magnetic susceptibility

A need for rapid and inexpensive methods of outlining areas exposed to increased pollution by atmospheric particulates of industrial origin caused scientists in various fields to use and validate different non-traditional (or non-chemical) techniques. Among them, soil magnetometry seems to be a suitable tool, at least in some cases. This method is based on the knowledge that detected higher values of magnetic susceptibility of soils' samples above background indicate higher concentration of heavy metals in soil (Strzyszcz and Magiera, 1998; Ďurža, 1999; Petrovský et al., 2000).

Measurements of magnetic susceptibility of topsoil have been successfully applied for mapping of degree of anthropogenic pollution near power plants, cement and metallurgy industries. All these studies demonstrate increased values of magnetic susceptibility of topsoil in contaminated areas compared to the signal of non-polluted soils.

Magnetic susceptibility of soil. The humus horizon is the most magnetic one. It is interesting that the concentration of heavy metals increases frequently with depth but the magnetic properties of heavy metal compounds decrease. It is in consequence of iron and other transient elements in a ferromagnetic state occur in this horizon and at the same time this trend is connected to the electron structure of non-ferromagnetic heavy metals complexes. These metals are assumed to have the highest concentration in the humus horizon where more kinds of organic ligands occur. These ligands are from humic and fulvic acids but also from other nonspecific soil organic compounds. The dependence of magnetic properties of heavy metal complexes on organic matters is explained by the ligand field theory, which was developed during the 1950s by the physicist J. H. van Vleck. This ligand theory is defined by Cotton - Wilkinson (1973) like a theory of an origin and a consequence of splitting of ions' inside orbits by their chemical surroundings.

However, the magnetic susceptibility of soil especially depends on the shape, size and concentration of ferrimagnetic minerals (maghemite, magnetite and the titanomagnetites) as well as on the method of measurement. Some non-ferromagnetic heavy metals also account for the increase of values of magnetic susceptibility as a consequence of the effect of humic and fulvic and nonspecific organic compounds in the humus horizon.

The origin of magnetic particles in the soil. Magnetic particles in the soil may be derived geologically from atmospheric sources, anthropogenic, if they are derived from industrial emissions, or biogenic in nature. The strong correlation between magnetic susceptibility and several heavy metal concentrations suggests a significant contribution to the magnetism from anthropogenic sources in the topsoil (Chan et al., 1998).

Ferrimagnetic iron oxide particles (mainly magnetite and maghemite) in fly ashes, originating during high temperature combustion of fossil fuels, are potentially the most significant source of anthropogenic ferrimagnetics found in the upper soil horizons (Flanders, 1994). Except

Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava 2003 ISSN 1335-096X

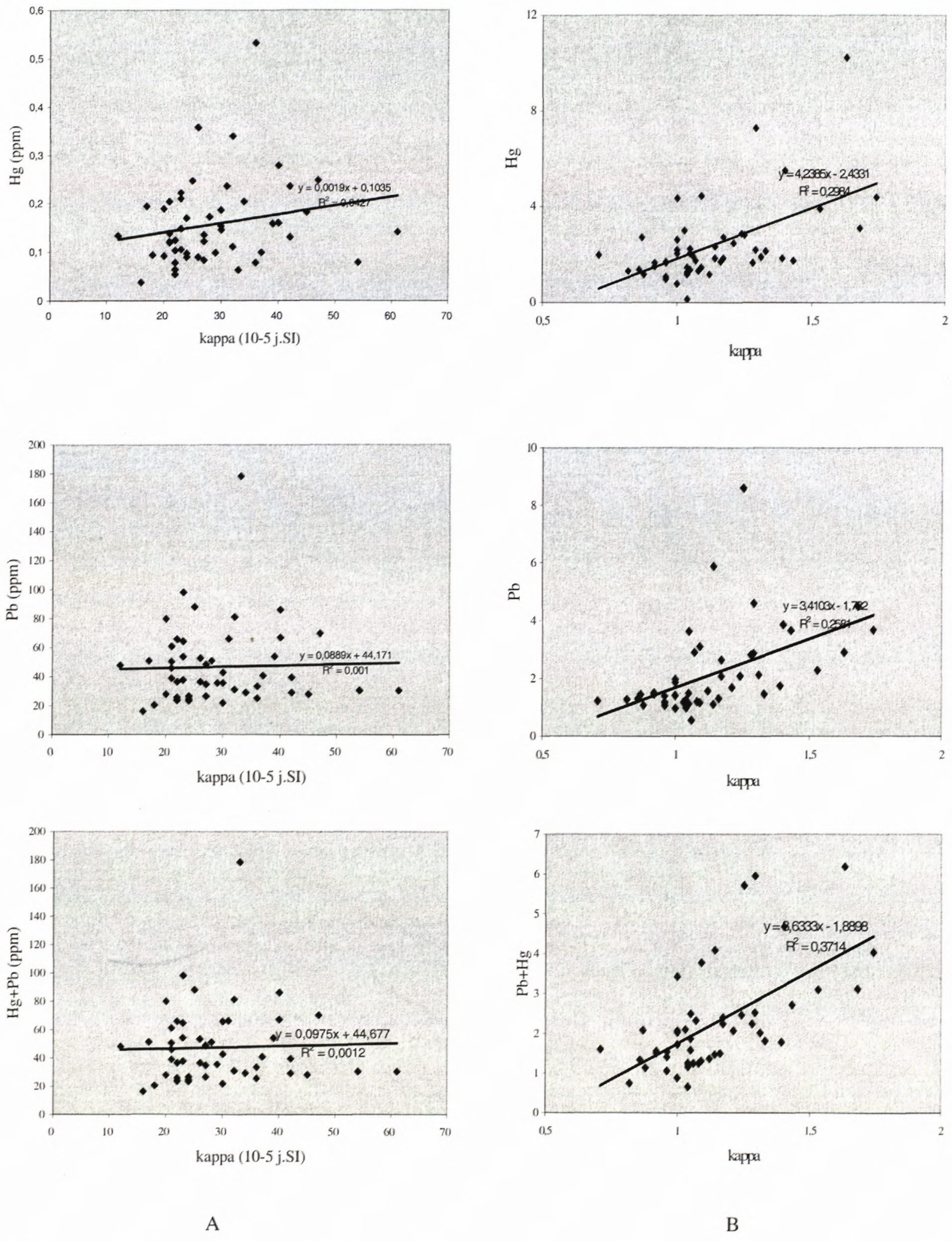


Figure 1 Comparison between absolute values (A) and RTE values (B)

for small amounts of magnetite in coal, the main source of ferrimagnetics is pyrite, the concentration of which reaches up to 15% of inorganic fraction in hard coal (Kuhl, 1961 in Magiera and Strzyszcz, 2000). Pyrite and other iron sulphides are oxidized during the coal combustion process. The sulphur is liberated as gas, whereas iron is converted into ferrimagnetic minerals, which are emitted into the atmosphere together with other dusts. The anthropogenic ferrimagnetics are transported as dusts and aerosols over variable distances to settle on the soil surface. Deposition of atmospheric particulates represents one of the most important contributions to environmental stresses.

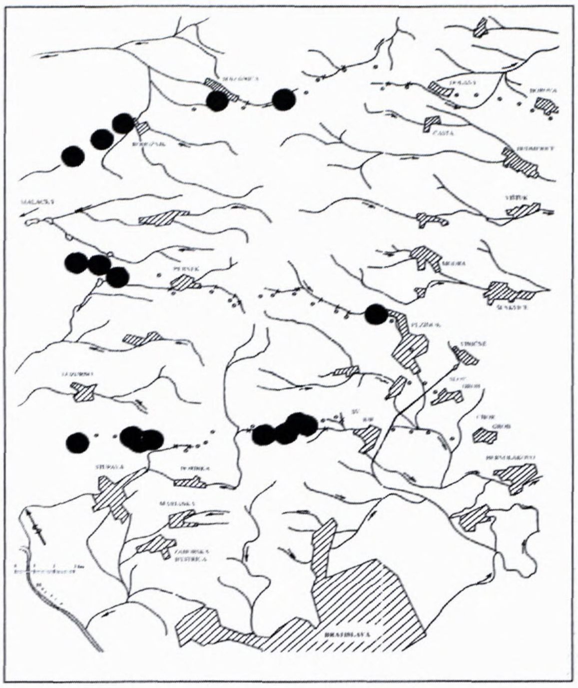


Fig. 2. RTE values of Hg+Pb+As+Sb > 2.0

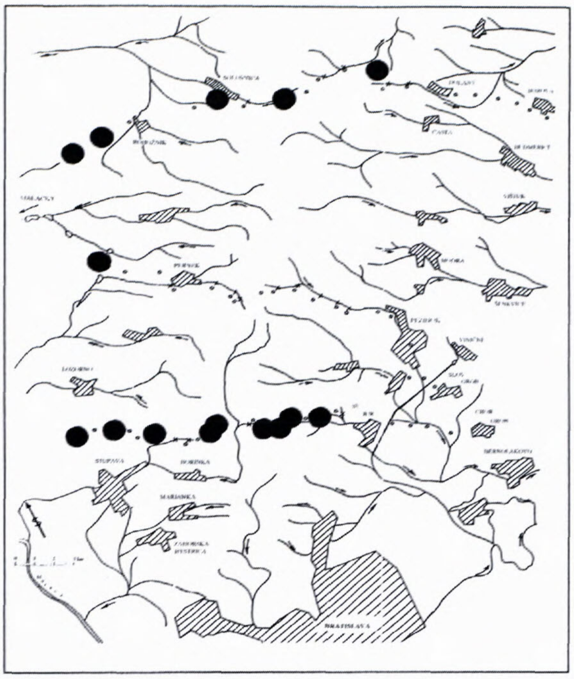


Fig. 3. RTE values of magnetic susceptibility > 1.2

The correlation between magnetic susceptibility and heavy metal content reveals a causal relation between ferric oxide and heavy metals. Previous studies have shown that certain heavy metals, such as Pb, Cu and Zn, are preferentially adsorbed onto the exterior surface of fly ash and aerosols from industrial emissions, which often contain significant amount of Fe and Mn oxides (Chan et al., 1998).

A strong correlation of these metals with the magnetic susceptibility is therefore expected. The coefficients of correlation between the magnetic susceptibility and the heavy metals contents are higher for Pb, followed by Cu and Zn and are weakest for Cr and Ni. The relative order of correlation for these metals with magnetic susceptibility can be explained in terms of the selectivity of clay minerals and hydrous oxide adsorbents for the metal, which generally follows the order Pb > Cu > Zn > Cr (Alloway and Ayres, 1993).

Cement production can also be considered as a major source of air pollution.

Another important source of atmospheric pollution, although limited in extent, is road traffic. In addition to Pb compounds, there are found hematite, magnetite and an iron aluminium silicate. As, Cd, Cr and Co are derived from the exhaust of automobiles and from tires as particles from tire ware. Furthermore, road surface (asphalt additives) represents another significant source of pollutants.

Detection of enhanced heavy metals levels in soil using magnetic susceptibility. It is known the measured values of soil magnetic susceptibility depend on parent rock of soil. In case of the homogeneous one this dependence does not cause the interpretation problems, e. g. magnetic susceptibility in soil around metallurgical plant U. S. Steel Košice (Ďurža, 1999). In case inhomogeneous ones these dependencies cause the interpretation problems, e.g. magnetic susceptibility in soils from Malé Karpaty Mts., because the measured values of soil magnetic susceptibility are higher above granites as carbonates and the highest are above ore mineralization. Since the aim was not to find the effect of substrata (geological) on soil magnetic susceptibility but the effect of topsoil contamination (anthropogenic), the relative topsoil enhancement (RTE) of elemental concentrations and values of magnetic susceptibility were used. RTE was the ratio of element concentration in topsoil (0--15 cm) to that in subsoil (30-45 cm) as an index of surface contamination (Colbourn and Thournton, 1978 in Alloway, 1990). In this manner the influence of parent rocks was taken off.

Measurements were taken along three profiles situated in the southwest part of Malé Karpaty Mts. There was measured magnetic susceptibility in two horizons - at the land surface and at the depth of 40 cm. There were measured and analysed 67 soil samples for these heavy metals contents: Pb, Hg, As, Sb, Cd, Fe, Ni, Co, Zn and Mn (Geological Institute, Faculty of Natural Sciences Bratislava, Slovak Republic).

The individual heavy metal is not possible to determine by soil magnetometry but their sum (soil's total burden of heavy metals) correlates with magnetic susceptibility values. RTE of contents of Hg, and Pb show relatively the strongest relation with RTE of magnetic susceptibility (+0.55, +0.51 respectively) (Fig. 2). Similar results were found in the surroundings of dry refuse heap of the U.S. Steel Košice and corresponded to Chan et al. results (1988), too. The highest values RTE of magnetic susceptibility and RTE of element contents occur in northwest slopes of Malé Karpaty Mts. and in the profile near Bratislava (Fig. 3 and 4).

Conclusion

1. The magnetic susceptibility values decrease with their distance from the source of contamination.

2. Enhanced magnetic susceptibility values occur in the uppermost part (humus horizon) of the soil profile and they decrease downward.

3. Changes of heavy metal levels in soils are accompanied with magnetic susceptibility values.

4. Values of a magnetic susceptibility of soils samples above background indicate higher concentration of heavy metals in soil, i. e. the soil magnetometry can be used like a preliminary quick and cheap method for the detection of a higher content of heavy metals in the soil.

Acknowledgements

The author is grateful to VEGA for their financial support (VEGA 1/9163/02).

References

Alloway, B. J. (Ed.) 1990: Heavy Metal in Soils. Blackie and Son Ltd., Glasgow and London, 339 p.

Alloway, B. J., Ayres, D. C. 1993: Chemical Principles of Environmental Pollution. Blackie Academic and Professional London, 291 p.

Brandau, A. and Urbat, M. 2000: Rock Magnetic Signature of Sediment near the Active Dead Dog Mound, Juan De Fuca Ridge. XXV EGS General Assembly, Geophysical Research Abstract, vol. 2, CD Rom.

Chan, L. S., Yeung, C. H., Yim, W. W. and Or, O. L., 1998: Correlation Between Magnetic Susceptibility and Distribution of Heavy Metals in Contaminated Sea-floor Sediments of Hong Kong Harbour. Environmental Geology 36(1-2), 77-86

Cocuaud, F., Roussaeu, D. D. and Antoine, P., 1998: Rock Magnetism as a Paleoclimate Proxy in the Loess at Nussloch, Germany. Annales Geophysicae, Part I, Suplement I to Volume 15, C 101.

Cotton, F. A. and Wilkinson, F. R. S., 1973: Inorganic Chemistry. Académia Praha, 1102 p. (in Czech).

Dlapa, P., Kubová, J., Medveď, J., Juráni, B. and Streško, V., 2000: Heavy metal fractionation in soils of different genesis. Slovak Geol. Mag. 6, 27-32.

Ďurža, O., 1999: Heavy Metals Contamination and Magnetic Susceptibility in Soils around Metallurgical Plant. Phys. Chem. Earth (A) 24(6), 541-543.

Kapička, A., Jordanova, N., Petrovský, E. and Ustjak, S., 2000: Magnetic Stability of Power Plant Fly-ash in Different Soil Solutions. Phys. Chem. Earth (A) 25(5), 431-436.

Magiera, T. and Strzyszcz, Z., 2000: Ferrimagnetic Minerals of Anthropogenic Origin in Soils of Polish National Parks. Water Air and Soil Pollution 124 (1-2), 37-48.

Mikľajev, J. V. and Žogolev, S. L., 1990: Relation between Magnetic Susceptibility and Lithogeochemical Dispersion Aureole of Ore Elements. Vest. Leningr. Un-ta, ser. 7, N 14, 26-33 (in Russian).

Milička, J., Vass, D. and Pereszlényi, M., 2002: Organic Matter Study from the Late Miocene Sediments of Lučenecká kotlina Depresion, Southern Slovakia. Mineralia Slov. 34(2), 93–98 (in Slovak).

Petrovský, E., Kapička, A., Jordanova, N., Knab, M. and Hoffmann, V. 2000: Low-field Magnetic Susceptibility: a Proxy Method of Estimating Increased Pollution of Different Environmental Systems. Environmental Geology, Springer Verlag 39(3-4), 312-318.

Strzyszcz, Z. and Magiera, T., 1998: Magnetic Susceptibility and Heavy Metals Contamination in Soils of Southern Poland. Phys. Chem. Earth 23 (9-10), 1127-1131.

Verosub, K. L., Fine, P., Singer, M. J. and Tenpas, J., 1993: Pedogenesis and Paleoclimate: Interpretation of the Magnetic Susceptibility Record of Chinese Loess-Paleosol sequences. Geology 21, 1011-1014.

Slovak Geol. Mag. ,9, 2 – 3(2003),145 – 147

Certification of Geological Reference Material

PAVOL LUČIVJANSKÝ

Geological Survey of Slovak Republic, Geoanalytical Laboratories,
Markušovská cesta 1, 052 40 Spišská Nová Ves

Abstract: This articel aims to provide a short information on the preparation and certification of geological reference materials. It summarises the key issues and the principles in area of planning of the project, procedures for sample preparation, methods for homogeneity and stability testing, certification exercise, assigning of uncertainty and gives information for final form of certificate according to ISO Guide 31, 2000.

Key words: certified reference material, homogeneity testing, stability testing

Introduction

Certified reference materials play an important role in geological laboratories to help analysts monitor their laboratory performance, verify the quality of produced data, and thus improve the comparability of measurement results. New analytical techniques with increased precision of measurement and legislative and trading requirements have caused that laboratories are becoming increasingly interested for new reference materials of higher quality.

Guidance for the preparation of reference materials is given in ISO Guides (ISO Guide 31, 2000; ISO Guide 34, 1996; and ISO Guide 35, 1989) and guides on the preparation of reference materials are also available (European Commission Document, BCR/01/97, 1997; B. Brookman et al., 1998).

According to ISO Guides 35 **Certified Reference Material (CRM)** is Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realisation of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

Preparation of reference material

Laboratory (producer) which intended to prepare CRM may submit a proposal for a project to Slovak Institute of Metrology which according to the Law No. 142/2000 for metrology has responsibility as a certification body for certification of RMs. The proposer in proposal have to take into account for which purpose or use should be CRM prepared. In the planning and during the designing of the project the producer has to identify a kind of matrix material to be collected, identification of suitable source and procedure for sample preparation, amount of material needed, definition of parameters, range to be certified, choice of the methods for homogeneity, stability and characterisation studies. The next part of the project is designing for ensuring storage, labelling, packing of CRMs, transport arrangement, post distribution services and design of a certificate.

After the identification of a suitable source of material producer has to decide about the amount of the material which should be collected. The amounts of material depend on the number of samples needed for commercial use, homogenity, stability study and what amount is needed for certification exercise.

The producer should take care of selecting a suitable processing procedure in order to prevent any contamination of material, change or degradation in the form, ensure that its final form achieve the required homogeneity and is sufficiently stable.

Typical procedures for processing of geological reference material are drying, crushing, grinding, quartering, sieving, testing of grine size and bottling. Before processing of geological reference material it is necessary to perform petrography – mineralogical characterisation and preliminary chemical analysis to obtain basic information about candidate RM.

The meaningful aspect that should be considered in the process of certification of geological RMs is that in generaly, certified compounds are related to dry matter and therefore the dry sample mass has also to be assessed. The moisture content has to be determined on a separate subsample to enable analytical results to be expressed on a dry sample weight basis. Choice of several competent and experienced laboratories which are able to perform the certification measurements play important role in the process of characterisation of RM. Performance of the participating laboratories is possible to assess through proficiency test on the samples which have approximately the same chemical and mineralogical composition as tested candidate reference material.

Homogeneity testing

The first step in the preparation of geological RMs is conducted with a homogenity test. The homogeneity test

Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava 2003 ISSN 1335-096X

is performed prior to certification on a reasonable number units (bottles) randomly selected from batch of bottles of candidate reference material that has been packed in its final form. There are two kinds of homogeneity study. Between unit variation (between – bottle homogeneity study) and within – bottle homogeneity study. From between – bottle homogeneity study is determined between – bottle variation as one important component of uncertainty which must be included in the total uncertainty of CRM (Thomas P. J. Linsinger et al., 2001). Within – bottle homogeneity study is necessary to determine a minimum representative sample portion which will be identical in terms of their certified properties and uncertainties.

The measurements for both homogeneity study should be carried out under best repeatability conditions, in one laboratory, in such a way to minimise possible drift in measurements. Applied measurement method should be selected for its good repeatibility. Recommended number of samples (depending on the type of material and repeatability of the method) is from 8 to 30 (European Commission Document, BCR/01/97, 1997). Analysis of variance (ANOVA) according to ISO Guide 35 should be used for statistical evaluation of homogenity study. An example for between – bottle homogeneity study is showed in Fig.1. This model is an ideal case where subsampling from selected bottles and multiple measurements after transformation is possible (Adriaan M. H. van der Veen et al., 2001).

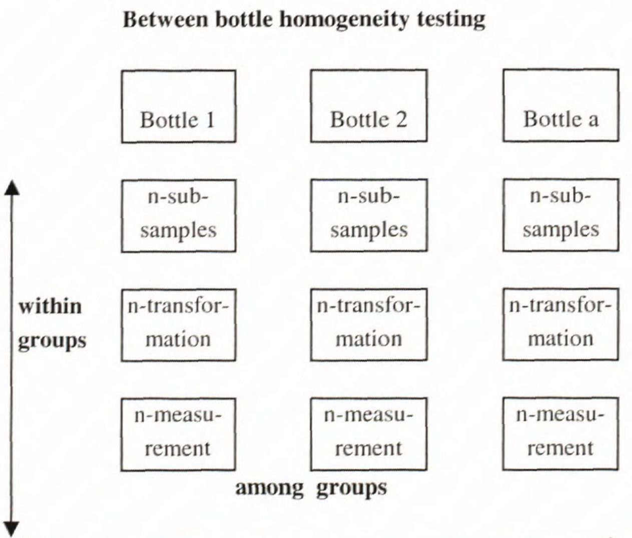


Fig.1 Between – bottle homogeneity study

Stability testing

The stability testing is second crucial point in characterisation of CRM. This testing can be performed when homogeneity of candidate reference material has been demonstrated. There are two types of stability testing, long term stability and short term stability. Long term stability gives an information about material that was exposed storage conditions and short term stability is associated with realistic conditions of transport.

The selection of testing condition will depend on the structure of the geological material and knowledge of behaviour of components of interest.

The frequency of testing for long term stability trials is usually 0, 3, 6 and 12 months and for a short term study is shorter period not longer than 4 weeks. Stored temperature of samples for long term stability is in general at room temperature and various temperatures (e.g., +4 °C, room temperature and 35 - 40 °C) are selected for short term study.

The measurement method applied for stability study, where the samples are analysed at different times should be choosen on the basis of its production of highly repeatable measurements.

Certification excercise

For the characterisation of geological matrix reference materials there are two approaches, first by a single method and second through the series of analysis carried out by multiple methods and laboratories. Second approach is mostly used through organized interlaboratory programme. The most important aspect for successful certification of candidate RM is that the organiser of interlaboratory programme should check if a group of competent and experienced laboratories in the area of analysis of geological materials is available to perform the certification measurements and if several independent methods are available. According to ISO Guide 35 the minimum number of participating laboratories is 15 or more.

The organiser should send to each participant one unit of RM with sufficient amount of material to allow the participant carry out minimum two replicate determinations, which should be made on separate test portion for all requiered certified properties and to use method of its choice. If the results from interlaboratory programme are to serve as a final confirmation of the homogenity of an RM, two units should be send to allow meaningful statistical processing of the results. For statistical treatment of data there exist many programmes and ISO guides which offer assistance. The results generated from Interlaboratory programme should be subjected to careful examination, outlieres thoroughly investigated and finally from these data certified value and its uncertainty are estimated.

The most important aspect in characterisation of RM is assigning final uncertainty of a CRM in which all sources of uncertainty should be considered. According to Guide to expression of uncertainty in measurement (GUM, 1993) the final uncertainty is expressed as:

$$u_{\mathrm{CRM}} = [u^2_{\mathrm{char}} + u^2_{\mathrm{bb}} + u^2_{\mathrm{lts}} + u^2_{\mathrm{sts}}]^{1/2}$$

where:

– u_{char} is uncertainty of characterisation of the batch which was described in publication by Pauwels et al., 1998 and which includes standard uncertainties which are exclusively laboratory dependent, common to all of laboratories, such as the effect of between-bottle variation or use common calibrant and standard uncertainty common to groups of laboratories (labs using the same measurement procedure),

- u_{bb} is between-bottle uncertainty,
- u_{lts} is uncertainty for long term stability,
- u_{sts} is uncertainty for short term stability.

At the end of certification procedure the producer should prepare a report, which should include a full account of the procedures used for the preparation and certification of the RM and prepare records for issue of certificate according to ISO Guide 31, 2000. The certificate should include minimum following information:

- name and address of the certifying organization,
- title of the document,
- name of material,
- sample number,
- description of RM,
- intended use,
- instruction for correct use of RM,
- state of homogeneity, stability,
- certified property values and their uncertainties,
- ucertified values,
- values obtained by idividual laboratories or methods,
- date of certification,
- date of expiration,
- signatures or names of certifying officers.

Conclusion

The preparation and certification of reference material consists of several principal componets. The producer of RM should start with responsible planning of the project, thorough knowledge mineralogical and chemical composition of the material, methods used for sample preparation, homogenisation and bottling of the material. The choice of highly repeatible methods applied for homogeneity and stability study, selection appropriate groups of competent laboratories for performing of the determination of properties of the interest, knowledge of the statistical methods which are used for assignment of the certified values and their uncertainties, all of this is needed for successful and complex realisation of the preparation and certification of RM.

References

ISO Guide 31: 2000 – Contents of certificates of reference materials.

ISO Guide 34: 1996 – General requirements for the competence of reference materials producers.

ISO Guide 35: 1989 – Certification of reference materials - General and statistical principles (under revision).

European Commission Document, BCR/01/97 (Sep 1997): Guidelines for the production and certification of BCR reference materials.

B. Brookman and R. Walker, Guidelines for the In-House Production of Reference Materials, July 1998, LGC Report, UK.

Thomas, P. J., Linsinger, Jean Pauwels, Adriaan, M. H. van der Veen, Heinz Shimmel, Andrée Lamberty, Homogeneity and stability of reference materials, Accred Qual Assur (2001) 6: 20-25.

Adriaan M. H. van der Veen, Thomas P. J. Linsinger, Jean Pauwels: Uncertainty calculations in the certification of reference materials. 2. Homogeneity study, Accred Qual Assur (2001) 6: 26-30.

Jean Pauwels, Andrée Lamberty, Heinz Shimmel: The determination of the uncertainty of reference materials certified by interlaboratory comparison, Accred Qual Assur (1998) 3: 180-184.

Slovak Geol. Mag., 9, 2 – 3(2003),149 – 152

Electron Microprobe Analyser (EPMA) – the Principles and Applications in Modern Geology

SIMAN PAVOL, KOLLÁROVÁ VIERA, KONEČNÝ PATRIK and HOLICKÝ IVAN

Department of Electron Microanalysis, Geological Survey of Slovak Republic, Mlynská dolina 1,
817 04 Bratislava, Slovak Republik

Key words: electron probe microanalyser, electron microprobe analysis, geology

Introduction

The principle of electron microprobe analysis was firstly described in 1947 by Hillier, (U.S. patent). He defined it as a chemical analysis using characteristic X-ray spectra excited by a focussed electron beam. In 1951 R. Castaing, under the supervision of Professor A. Guinier at the University of Paris, wrote his Ph.D. thesis, where he presented the foundations of the theory and practice of quantitative electron microanalysis. He described the successful development of a new instrument destined to have an impact in many fields of science and technology. The instrument originated by join of classical electron optics and electron microscope with fitted X-ray spectrometer. It was called *the electron microprobe* or *the electron microprobe analyser (EPM - EPMA).* The first commercial instrument was developed in Paris, France by the Cameca Company, in 1958 (Reed, 1997).

The methods of electron microprobe analysis have its important place also in Slovak geology. The first EPMA JEOL - 733 Superprobe was bought in 1981. It was used 20 years, since 1981 to 2001, at Geological Survey of Slovak Republic (GÚDŠ, GSSR) Bratislava. This instrument was rebuilt and modernised in 1992 - 1995.

JEOL JXA - 733 SUPERPROBE was the electron microanalyser with four WDS spectrometers with crystals TAP, PET and LIF, controlled by KEVEX SESAME system and KEVEX DELTA+ EDS spectrometer with software package QUANTEX+. There were produced plenty of WD and ED analyses, BEI and SEI images.

In 2001, this old instrument was replaced by the CAMECA SX-100 electron microanalyser, which represents one of the most modern instruments used for the investigation of geologic, but not only geologic materials. In almost two years of full service, it persuades about its important place in the Slovak geology.

Principle of electron microprobe analysis

Electron microprobe analysis is a non-destructive analytical method for chemical analyses of small volumes of solid samples. Accelerated electrons in the form of a finely focused electron beam (probe) bombard a polished sample. X-rays are excited by the interaction of this electron beam with atoms of the sample. The place of this interaction is very small (usually some μm) so we can name it as the *analysed point.*

The versatility of this method among material sciences is based on its simplicity. X-ray spectrum is mostly independent on a physical and chemical state of studied material and it directly depends only on the atomic number of the present elements. The X-ray spectrum contains lines which are characteristic of the elements present, hence an analysis is easy to obtain by identifying the lines from their wavelengths or photon energies.

Electron microanalysis can be performed with two systems. In ***Wavelength dispersive method*** *(WD)* X-ray of defined *wavelength* corresponds to certain element. Generated X-rays are diffracted on crystals and then detected by a detector. The position of crystal and detector on Rowland circle follows Bragg´s law. In ***Energy dispersive method*** *(ED)* X-ray with defined *photon energy* corresponding to certain element is detected by so called Si(Li) detector. Since 1968 the solid-state Li-drifted silicon detector is known and widely used for detection of low energy X-rays.

Qualitative analysis serves for identifying of elements present in the sample. In this case X-ray spectrometer records the whole spectrum over the range of wavelengths (WD method) or energies (ED method). Lines and energies of present elements in acquired spectrum are identifiable by the reference to tables.

In *quantitative analysis* the intensities of X-rays correspond to the concentrations of elements present in studied material. In the case of WD method, the intensities are detected in counts per time. In ED method, the intensities are detected also in count per time, but for the certain energy window (in eV).These intensities are compared with intensities from standards of known composition (pure elements, natural and synthetic compounds). According to known standard composition we can calculate composition of the studied material. We need to make number of corrections to the measured data to obtain a precise analysis, e.g. substraction of background, "matrix corrections". ZAF correction which takes into account correction factors depend on atomic number, absorbtion and fluorescence is widely used (Reed, 1997).

Other applications of EPMA

EPMA yields not only information about the composition of samples but also image observations. Images from EPMA are comparable with those acquired from classical scanning electron microscope, but with less magnification and resolution. Images are created by the scanning electron beam in a television-like raster and displaying a collected signal from the detector on the screen. Scanning electron beam interacts with sample surface to produce various types of signals (Fig. 1). A specific type of image corresponds to specific type of signal (secondary electrons, back-scattered electrons, cathodoluminescence).

Secondary electron images (SEI) give us information about sample surface. Secondary electrons are weakly bounded electrons released from the surface of the sample. ***Back-scattered electron images*** (BEI) give us approximate information about the composition of the sample, darker places at these images contain elements with lower atomic number and vice-versa. The back-scattered electrons are electrons of beam scattered out from the sample after interaction with atom core. The higher atomic number of element, the more of interactions which produce these electrons. ***Cathodoluminescence*** is based on the detection of visible light which is also generated by interaction of electron beam with the sample. Cathodoluminiscence is observable only in some materials e.g. quartz, feldspars etc. Cathodoluminescence images are used for identification of inner texture, small veins, cracks, growth zonation.

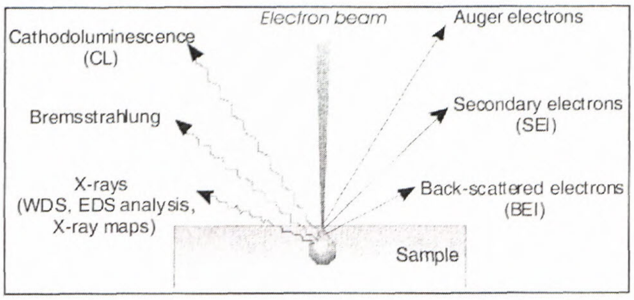


Figure 1. Interaction between electron beam and sample gives an origin to the various types of signals, which can be detected and used in electron microscopy and microanalysis. The space of interaction has an onion shape. (Compiled by V . Kollárová according to Energy - Dispersive X-ray microanalysis. An Introduction. Kevex Instruments, Inc., 1989, 52 p.)

The main construction principles of EPMA

An electron microprobe (Fig. 2) consists of the main frame with column and spectrometers, then of block of electronics, cooling system, vacuum system and controlling computer.

The electron beam is generated and corrected in the vertical column positioned on the main frame. It consists of electron gun, alignment coils, condenser lens, probe current detector, aperture, scanning coils, stigmator and objective (final) lens. The electrons are produced thermoionically from heated tungsten filament in the top of the column. They pass through Wehnelt (focusation elect-

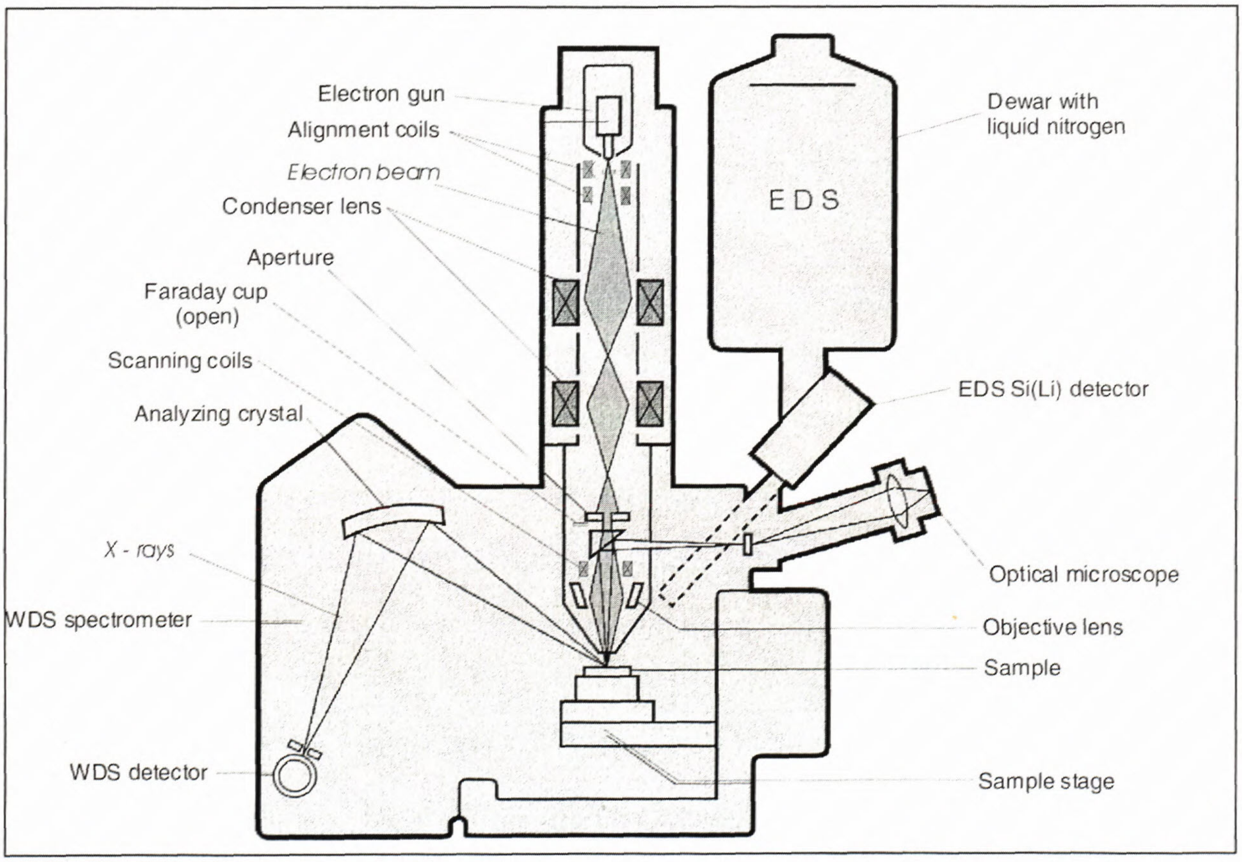


Figure 2. Schematic diagram of electron probe microanalyser. Electron gun consists of filament, Wehnelt and anode. (Compiled by V. Kollárová and P. Siman according to propagation materials of fy. JEOL).

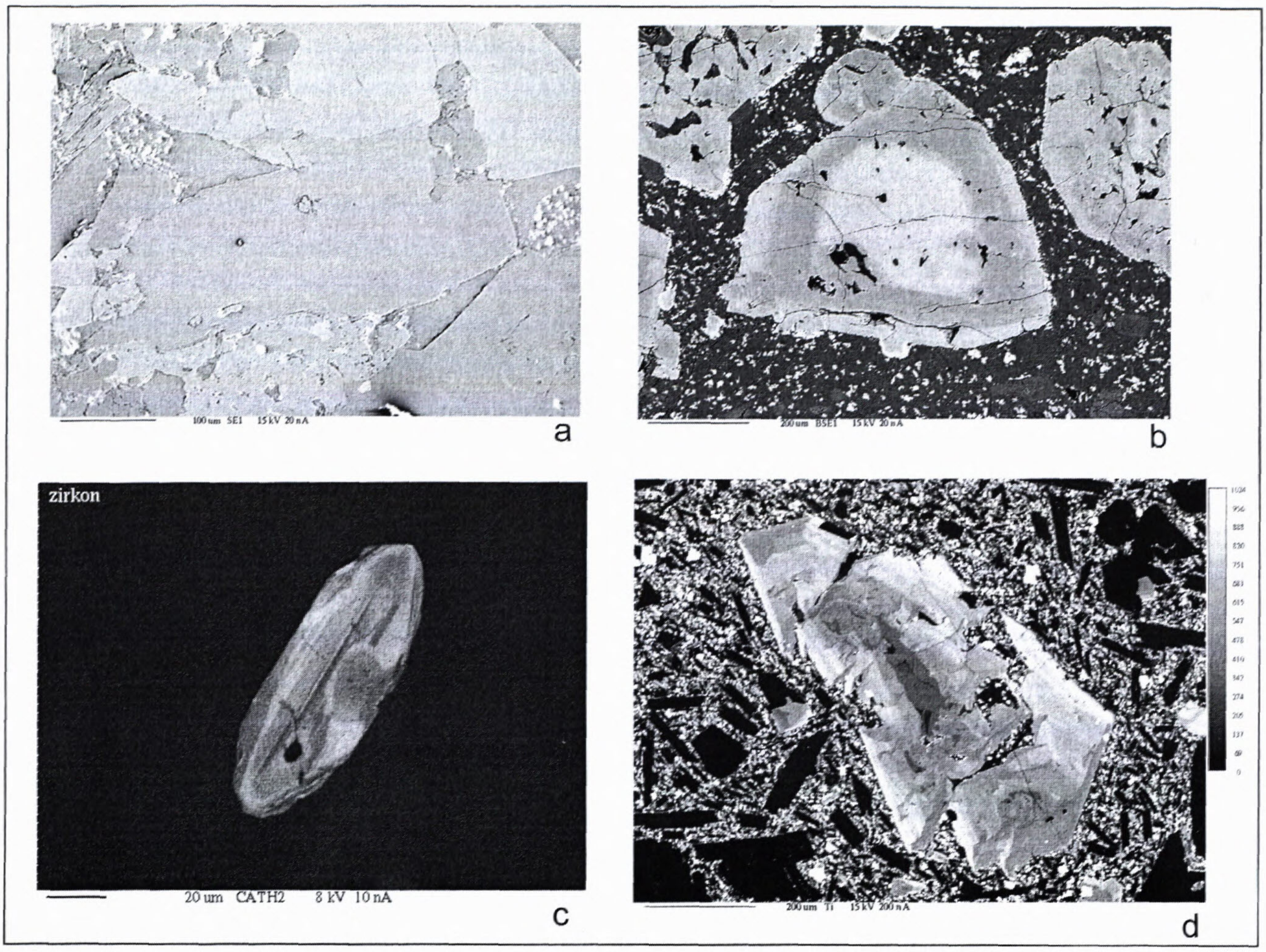


Figure 3. - Images taken by electron microprobe CAMECA SX-100 at Slovak Geological Survey, Bratislava
a - secondary electron image, porphyric quartz diorite, Javorie Mts., b - back-scattered electron image, zoned clinopyroxene, basaltic andesite, Kremnické vrchy Mts., c - cathodoluminescence image, zircon in stromatitic migmatite, Slovenské rudohorie Mts. d - X-ray map, distribution of Ti in zoned clinopyroxene, alkaline basalt, Banská Štiavnica

rode) and grounded anode. Electrons are speeded up by accelerating voltage 5 to 40 kV applied between a filament and anode. The electron beam is then collimated and focused by a system of magnetic lenses, apertures and coils. Prepared electron beam with specific beam diameter is used for analysing. Scanning coils are used for electron beam deflection to produce various types of images. The sample stage for fitting standards or samples is placed in the bottom of the column. Up to 5 WD spectrometers can be attached to the column. Inside we find the moving analysing crystals and detectors. Optionally we can add an ED detector. The sample inside in the column can be observed by optical microscope, usually with CCD camera. The block of electronics control the whole instrument including cooling system, vacuum system, electron optics etc. In advanced instrument all data are collected in computer.

EPMA in the laboratory of Geological Survey of Slovak Republic

The Department of Electron Microanalysis in the Geological Survey of Slovak Republic is equipped with electron microprobe analyser CAMECA SX-100. This instrument is a representative of the new generation of microprobe in the most modern and unique laboratory of this type in Slovakia. Here are some basic parameters:

- three built-in vertical spectrometers with large analyzing crystals LLIF, LPET, LPCO and TAP, PC2
- energy-dispersive (ED) spectrometer KEVEX with ultra-thin window Moxtek AP 1.3
- SEI, BEI and cathodoluminescence detector for images
- very stable electron beam (beam stability 0.3% in 12 hours)
- very precise system of movement of the versatile specimen stage
- optoelectronics, which controls stage, detector and crystals
- coaxial optical zoom microscope with autofocusing colour CCD camera, field of view 0.25 – 1.7 mm, polarized light
- SUN microsystem operating basis

The analytical possibilities are summarised as follows:

- wavelength-dispersive (WD) analyses from *boron* to *uranium* with routine precision 0.01 wt. %

- semiquantitative and quantitative energy-dispersive (ED) analyses from *fluorine* to *uranium*
- line profiles with stage or beam movement
- X-ray mapping
- high-quality BEI and SEI images with resolution up to 2048x1536 pixels
- cathodoluminescence images
- all results available in digital and printed form

Geological applications of EPMA

Methods of microanalysis and image analysis are commonly used in geology, basic and applied research. It is a non-destructive method for analysing samples of rocks and minerals with maximum spatial resolution of ~ 0.7 mm. Rock samples must be perfectly polished. We can mount thin sections (2.5 x 4.5 cm) and cross sections (diameter of the cylinder 2.5 cm) in the sample holder. The polished samples must be carbon coated under the high vacuum. Individual mineral grains can be analysed in situ, with their structural and textural relationships. Samples can be observed in an optical microscope as well as under scanning electron beam which enables us to localise the mineral phases, relationships among them and finally, a position of the suitable place for the microprobe analysis. SEI, BEI, CL, optical images (Fig. 3) and all measured data can be easily saved in computer in digital form or directly printed or sent by E-mail.

The accuracy of analysis is routinely under ~0.01 wt % depending on the concentration of the element in the sample. 1s error (wt %) is directly listed in the analysis report. In special cases the detection limit ~ 50 ppm (100--10 ppm) is possible to achieve. All elements with atomic number above 9 (F) can be determined with uniform accuracy and sensitivity. Measurement of lighter elements requires a special care and conditions.

Sample exchange is very easy and requires a relatively short time. Also one silicate analysis (10 elements) is completed quite quickly, in ~ 3 minutes. It is enabled by special large analysing crystals that are approximately 8-times more sensitive then the classical ones.

All above mentioned microprobe analyses and image pictures including X-ray maps are well usable in the mineralogy, for finding a mineral composition, growth profiles, diffusion profiles, potentially for a finding of new mineral species, then in descriptive and experimental petrology for the geothermobarometry calculations, rare phase location, investigations of mineral successions and relations among minerals and approximate modal analysis.

Our possibilities and experience with electron microprobe analysis

During 20-year history of electron microanalysis methods usage in our Institute, we have attained many experiences with chemical analyses. Our possibilities and experiences can be summarised as:

- basic chemical compositions of the rock-forming, clay and accessory minerals
- ore and silicate deposit minerals, including composite sulphosalts and sulphides
- micro, trace and rare earths element measurements
- environmental problems - wastes, heavy metal and asbestos distribution
- different kinds of geological problems
- analyses of the crushed stones, construction and decoration stones

References

Reed, S. J. B., 1997: Electron microprobe analysis. Cambridge Univ. Press, Cambridge, 326 p.

Slovak Geol. Mag., 9, 2 – 3(2003) 153 – 156

Analytical, Organic, Microbiological, and Hydro-Biological Methods Used in Surface Water Quality Evaluation in Slovakia

RENATA REPKOVÁ, ĽUDOVÍT BRUNDZA, VIERA LUČIVJANSKÁ and PAVOL LUČIVJANSKÝ

Geological Survey of Slovak Republic, Geoanalytical Laboratories,
Markušovská cesta 1, 052 40 Spišsská Nová Ves

Abstract. This article concerns the information about the monitoring of surface water of Slovakia which is performed every month at 157 places of four river basins. Analytical, organic, microbiological and hydro-biological determinations are performed in Geoanalytical Laboratories of Geological Survey of Slovak Republic, Spišská Nová Ves. All the methods which are used for determinations are validated, accredited and they are checked by the participation in the interlaboratory comparision. The results are provided for Slovak Hydro – Meteorological Institute in Bratislava which is by the Ministery of Environment in charge of setting – up the monitoring of surface water and of the evaluation of results.

Key words: surface water, river basin district, surface water quality, organic factors, bacteria, control of analytical date

Introduction

Monitoring of Ecological and Chemical State of Surface Water

The surface water quality of Slovakia has been monitored systematically since 1963.

In 1982 the Slovak Hydro-Meteorological Institute in Bratislava took the role of monitoring the quality of surface water in Slovakia. They set up a monitoring network that provides a complete and organized survey of ecological and chemical state of every River Basin District, and they divide water formations into five quality classes. Monitoring sites are selected where a sample of water is representative for an entire basin.

The main goals of this network are to determine the current state of surface water quality in Slovakia, to identify and to quantify the main sources of pollution, to evaluate the trends of surface water quality development in Slovakia, to provide information for The Ministry of Environment of Slovakia and water-economic offices for their decision process, and to use the analyses for expert research and reports.

Monitoring Network

The total length of rivers with basins over 5 sq kilometers is 24.777 km. The monitoring of surface water quality is done in four basins – the Vah, the Hron, the Danube, and the Bodrog and the Hornad. There are 157 testing locations in all. Since 2001, surface water analysis has been provided by Geonalytical Laboratories, accredited testing Laboratories of Geological Survey of Slovakia.

The basic method of evaluating surface water quality is to classify the surface water according to STN (Slovak Technical Norm) 75 7221, which establishes five classes of water quality:

1. very clean water, 2. clean water, 3. polluted water, 4. strongly polluted water, 5. very strongly polluted water. Monitoring parameters of surface water can be divided into two groups, tab. 1:

Basic factors – which are determined in all testing locations twelve times a year.

Additional factors – which are determined only in specially selected river basin sources, and less frequently.

Table 1. Monitoring parameters of surface water

Basic factors	Additional factors
dissolved oxygen, % dissolved oxygen	total nitrogen
BOD, COD	PO_4^{3+}, HCO_3^-, CO_3^{2-}
total dissolved solids, suspended solids(dried, ignition)	phenol Index- FNI, anionic surfactants, total cyanide
Chloride,sulfate, total alkalinity	chlorophyl "a"
NH_4^+, NO_3^-, NO_2^-, total phosphor	Ca^{2+}, Mg^{2+}, Na^+, K^+
Saprobic index	Fe, Mn, Cr, Cu, Zn, Cd, Pb, Ni
Coliformn organism	Hg, As, Al,
	total volumetric activity alpha and beta, Sr, Ba
	Organochloride Pesticide
	Volatile Halocarbons
	Polynuclear Aromatic Hydrocarbons
	Polychlorinated Biphenyls
	Triazine Herbicides
	Cyclohexanol, Cyclohexanone
	Formaldehyde

Analytical Methods Used in Evaluation of Surface Water Quality in Slovakia

Basic Physical-Chemical Factors

Proper sampling and storage of water is essential for accurate results. All water samples are evaluated according to STN norms. Sample parameters (elements and properties) which could change during transportation have to be determined in situ (pH, water temperature, dissolved oxygen). Sample parameters which change have to be also preserved by adding special chemical reagents upon extraction. Cyanids and fenol volatized with water steam are preserved with NaOH to pH 11, to avoid their loss. Ca, Mg, Na, K, Fe, Mn, Cu, Cr, Zn, Ni, Pb, Cd, Hg, As, AL, Ba are fixed after filtration by 5ml/l of HNO_3 to avoid their precipitation. P_{total} is preserved by adding 2 ml/l chlorophorm and has to be kept at temperature from 3 to 4 ^{0}C till the expertise. On the day of sampling it is necessary to measure ammonium and nitrites to avoid their oxidation or reduction.

Biochemical oxygen demand must be determinated within 24 hours because the biggest reduction of oxygen occurs in the first 24 hours and the results measured after this time will not be accurate. Within 24 hours of sampling it is also necessary to measure electrical conductivity, phosphates, nitrates, total dissolved solids. If chemical oxygen demand cannot be determinated within 24 hours, the sample water has to be conserved with 2 ml/l of H_2SO_4, and kept at 3-4 ^{0}C. Within 48 hours after extraction, it is possible to determinate chloride and sulfate but the samples have to be kept at 3-4 ^{0}C.

Analytical methods of measurement can be divided into the following groups:

1. spectrophotometric methods – determination of NH_4^+, NO_2^-, PO_4^{3-}, $P_{tota.}$, $N_{total.}$, FNI, CN, COD, anionic surfactans,
2. volumetric method – the determination of total alkalinity,
3. ion chromatography – the determination of Cl^-, NO_3^-, SO_4^{2-},
4. gravimetric method – the determination of solids (dried and ignited),
5. oximetry – the determination of BOD,
6. ICP-AES – inductively coupled plasma atomic emission spectrometry – the determination of Ca, Mg, Na, K, Fe, Mn, Cr, Cu, Zn, Cd, Pb, Ni, Al, Ba, Sr,
7. HG - AAS – hydride generation atomic absorption spectrometry - the determination of As,
8. AAS – atomic absorption spectrometry – the determination of Hg
9. Counting – the determination of HCO_3^-, CO_3^{2-}

Monitoring of Organic Compounds

The amount of organic compounds in the hydrosphere is growing and so has their harm to the environment. The main cause of artificial organic pollution is chemical waste, due to human activity. Organic pollutants are harmful for surface water quality, have the ability to remain in the environment for long periods of time, to disperse widely, and to accumulate in tissues hurting the environment and its inhabitants, even in small concentrations.

Organochloride pesticide (OCP) – chemical substances or their mixtures used mostly in agriculture against organisms that harm cultural plants or are harmful to humans.

Volatile Organic Halocarbons (VOC) – chlorinated organic materials are used such as additives to colours or plastics, adhesives, for producing of plastic materials, for desinfection materials, bleach and solvents.

Polynuclear Aromatic Hydrocarbons (PAH) – a group of materials with two or more bensen nucleus. Basic Polynuclear Aromatic Hydrocarbons are the following sixteen compounds: naftalene, acenaftylene, acenaftene, fluorene, pyrene, fenantrene, antracene, fluorantene, chryzene, benzo (a)antracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h) antracene and benzo(g,h,i)perylene.

Polychlorinated biphenyls (PCB) – the complexity of PCB mixture and their thermal breakdown products are toxic for environment and people. PCB were added into paints, transformer and condenser oils, plastic matters and caoutchouc.

Triazine herbicides – chemical materials used mostly in agriculture as OCP.

Sampling

The samples of water are taken into glass bottles and kept at 4 ^{0}C.

They are not conserved.

Determination of organic compounds

Extraction methods, methods of analyses and detection limits of monitored organic groups are shown in the following table 2.

Table 2. Analytical methods, extraction methods and detection limits of monitored organic groups.

Substance	Type of extraction	Method	Detection limit (ug.l^{-1})
OCP	Solid phase extraction	GC/ECD	0,003-0,03
VOC	Purge&Trap	GC/FID	0,01-0,03
PAH	Solid phase extraction	GC/MSD	0,003-0,03
PCB	Liquid liquid extraction	GC/ECD	0,003
Herbicides	Solid phase extraction	GC/MSD	0,02

Microbiological and Hydro-Biological Evaluation of Surface Water

Microbiological analysis of surface water consists of Quality Classification, which means the identification of harmful bacteria and Quantity Classification, which means the exact amount of bacteria.

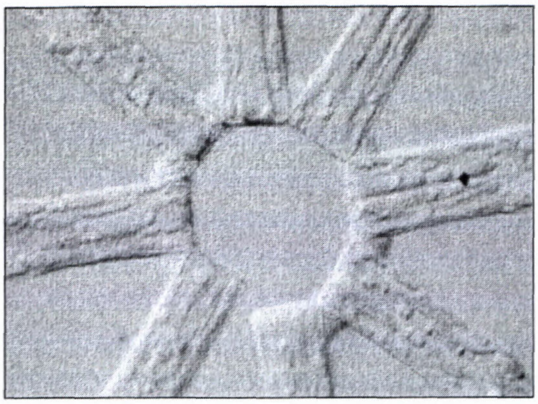


Figure 1: Tabellaria flocculosa – bacillariophyceae, microscopic, one-celled organism living in clean water.

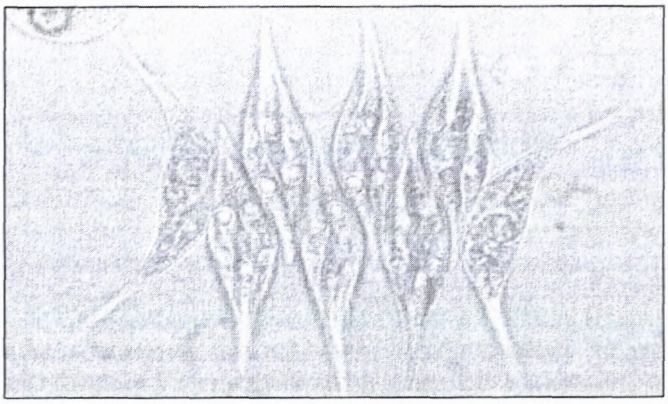


Figure 2: Scenedesmus acuminatus – green, cenoby river weed with cells in two rows that lives in plankton and in river bank of moderately clean water.

In surface water were determined these groups of organisms:

- Detection and enumeration of coliform organisms, thermotolerant coliform organisms.
- Detection and enumeration of faecal streptococci.
- Microbiological analysis of surface water. Total plate count at 37°C and at 20°C.

Microbiological analyses identify the groups of bacteria that indicate the presence of faecal from both private homes and industrial complexes. The presence and concentration of these contaminants measure the degree of water pollution and their hygienic level.

Hydro-Biological analysis consists of:

- Determination of saprobic index.
- Spectrometric determination of the chlorophyl-a concentration.

The content of organic saprogenic compounds, which are the nutritive source for other microscopic one-or-more-celled organisms, is determined by hydro-biological analysis of surface water. Microscopic identification and measurement of these agents is a basic step in the determination of water quality.

The presence and concentration of particular groups of microorganisms can indicate the current stage of water pollution. By hydro-biological parameters we monitor the ecosystem – all the organisms in our environment and how they interrelate. The results of microbiological analyses determine the cleanliness of surface rivers. By their regular monitoring we also monitor the environment in which we live.

Quality Control of Surface Water

The goal of every analytical laboratory is to produce reliable experimental results which guarantee high qualitative level and which are comparable with other laboratories. Providing such a level depends on all laboratory activities, starting with sample preparation, its analysis and finally making of a protocol. Each step could be a possible source of errors. Quality assurance and quality control must be elaborated to control each step of analytical procedure and therefore minimalize producing of random and systemetic errors.

Quality control of analytic data is assured on two levels: Internal an External control.

Used analytical techniques are regularly verificated by meteorological characteristics such as precision and accuracy of measuring, stability of signal, amount of noise e. g. Long term stability of analytical signal is monitored and evaluated by a regulation diagram.

1. Internal control of quality (IK) is provided by analysis of reference materials, multiplying analysis of sample from the same location, analysis of sample that was sampled twice from the same place and analyzed simultaneously.

2. External control of quality is provided by the national and international interlaboratory comparisons tab. 3.

Table 3. External control

Matrix	Measurements	Organizer
water drinking **surface** **waste**	– basic physical and chemical analysis – trace elements – special organic analysis – ecotoxicological tests – microbiological tests – hydrobiological tests	
water drinking	– trace elements	PIG Varšava, Poľsko
water drinking	– trace elements – basic physical and chemical analysis	VKI Hornsholm, Dánsko

Tests are performed for basic physical-chemical analysis, the determination of metal and organic parameters in surface water, and for the evaluation of hydro-biological and microbiological analysis of surface water.

The evaluation of results of IK control samples is performed by statistical analysis of comparing files of duplicate analysis, for each parameter separately. The result of evaluation is provided in graphical form. An example of graph of comparing values of test and control samples for nitrate is showed in Figure 3.

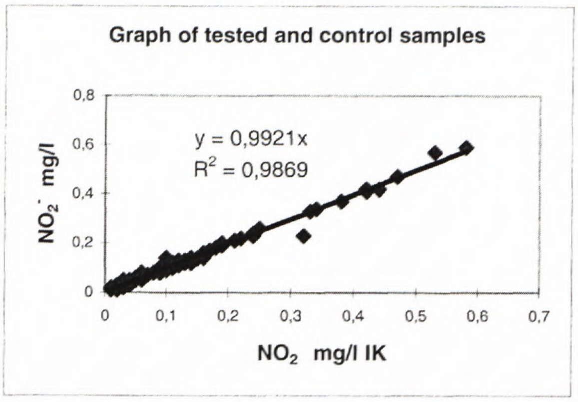


Figure 3. Graph of comparing values of test and control samples for nitrite

Conclusion

Nowadays Slovakia is trying to become a member of European structures and that is why it will be necessary to harmonize all used analytical methods applied in monitoring of surface and underground water to obtain comparable results. To achieve this goal the system of quality and further education of employees are needed to be improved.

References

STN 75 7221 Water Quality. Classification of Surface Water Quality, (1999).

Slovak Geol. Mag.,9, 2 – 3(2003), 157 – 159

The Evaluation of Precision and Trueness of Some Water Analysis Procedures in the Laboratories of Czech Geological Survey

LUDMILA DEMPÍROVÁ

Czech Geological Survey, Klárov 3, 118 21 Prague 1

Abstract. In the present contribution the practise of CGS laboratory in expressing precision and trueness of some water results is dealt with. Precision and trueness represent basic metrological parameters of an analytical method. For this evaluation, sets with QC samples or CRMs are used. Precision is characterized by standard deviation and relative standard deviation. Trueness is expressed by a difference from a true value and by recovery of a CRM.

The assessment steps are shown on the aluminium results acquired by atomic absorption spectrometry with electrotermic atomization, on pH measurement performed by a glass electrode, on conductivity measurements, on analysis of chlorides, nitrates and sulphates, determined by ion chormatography and on analysis of fluorides, determined by ion selective electrode.

Precision of conductivity measurements of rainfall samples is evaluated also by standard deviation and relative standard deviation calculated from duplicate samples rather than from QC samples.

The values of inner laboratory precision are compared with the precision values published in standard methods, relating to water quality in the Czech republic.

Key words: Analytical method, assessment of precision and trueness, criteria of an analytical method fit for purpose, suitability of a method for application.

Quality systems that are introduced in chemical laboratories, demand permanent check of analytical results. Practising checks on the calibration solutions and monitoring an error-free operation of an analytical instrumentation are desirable for an appropriate method control. Good proficiency information can be obtained from quality control (QC) samples as well as from different sorts of reference materials (RMs). Repeated measurements of samples (duplicates) belong to valuable assuarance outcomes, too.

Attention of a laboratory, paid to its controlling function, should lead to the declaration that the methods used by laboratory are of satisfactory accuracy. Quality assuarance (QA) measurements offer many repeatedly analysed QC samples that can be effectively evaluated and permit to make conclusions about trueness and precision of a method in use.

Trueness of a result can only be evaluated from a set of data with well defined mean value. Certified reference materials (CRMs) perfectly fulfill this requirement. Their assigned values are confirmed by a certificate issued by the certifying body. Reference values of QC samples can be derived from the mass and the volume, in which QC sample is dissolved.

An acceptable approach for assessing trueness is the expressing a difference of the analytical result and the certified value of a CRM. Further information about trueness of the results provides the value of recovery that is achieved by a tested analytical method on a CRM or a QC sample as well.

Table 1: Information data about QC samples used for precision trueness evaluation of some water analysis procedures

Element/ quality	Type of a sample	Laboratory mean value	Assigned value
Al	CRM BCR609 natural water	50.3 µg/L	47.7 µg/L
pH	CRM-buffer from Merck	6.86 pH	6.86 pH
Conductivity	CRM-conduct. std.from Alfa Aesar	725 µS/cm	718 µS/cm
Cl^-	Laboratory QC synthethic	2.66 mg/L	2.70 mg/L
NO^{3-}	Laboratory QC synthethic	6.55 mg/L	6.50 mg/L
SO_4^{2-}	Laboratory QC synthethic	16.49 mg/L	16.30 mg/L
F^-	Laboratory QC synthethic	0.67 mg/L	0.70 mg/L

The following equations (Standard Methods, 1998) are used for calculation a difference (% D)

$$\% D = \frac{found\ value\ - true\ value}{true\ value} * 100\% \quad (1)$$

and recovery (% Recovery) from values given by table 1

$$\% \mathrm{Re}cov ery = \frac{found\ value}{true\ value} * 100\% \quad (2)$$

The results of calculation are given in table 2.

Table 2: Error assessment in the control samples

Element/quality/ Analytical method	D %	Recovery %
Al/ET AAS	+ 5.5	105.5
pH/Glass electrode	± 0.0	100.0
Conductivity/CDM	+ 1.0	101.0
Cl^-/IC	- 1.5	98.5
NO_3^-/IC	+ 0.8	100.8
SO_4^{2-}/IC	+ 1.2	101.2
F/ISE	- 4.3	95.7

Legend: ET AAS – atomic absorption spectrometry with electrotermic atomization; CDM – conductivity meter; IC – ion chromatography; ISE – ion selective electrode.

Difference D (%) was calculated according to the formula (1), recovery according to (2).

The highest difference achieves +5.5% (determination of aluminium in water, see table 2), which at the same time corresponds to the recovery of 105.5% in the CRM BCR 609. If we regard ±5.0% difference as acceptable for good laboratory method performance then from this point of view the determination of Al by atomic absorption spectrometry with electrotermic atomization reaches the worse score.

The number of control data, the mean laboratory values in table 1 are calculated from, is between 20-40 elements. For quantifying precision of individual data sets, that contain repeated measurements of a specific QC sample, both standard deviation (3) or relative standard deviation (4) can be applied.

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \qquad (3)$$

$$\% \, RSD = \frac{s}{\bar{x}} * 100 \, \% \qquad (4)$$

Standard deviation s is calculated according to the equation (3), relative standard deviation RSD according to (4).

The conclusions about laboratory methods precision that were used for the determination of Al, pH, conductivity, anions (Cl^-, NO_3^-, SO_4^{2-}) and fluorides (F^-) were drawn from the comparison with the data precision information of standard methods, that are valid in the Czech republic in the field of water analysis now (see table 4). Water examination methods of a laboratory can be regarded as standard methods suitably modified at laboratory conditions.

The laboratories of Czech geological survey achieve an european standard in water analysis in the determination of pH (method glass electrode) and in the determination of SO_4^{2-} (method ion chromatography) – see tables 3 and 4. For the rest of the examined methods, their precision parametres are slightly worse, but nevertheless, these precision parameters still meet the laboratory's requirement on the declared quality.

Table 3: Precision assessment in the sets of control samples

Element/quality	Analytical method	Std. deviation	Relative std. deviation
Al (50.3 μg/L)	ET AAS	*	12.0 %
pH (6.86)	Glass electrode	0.02 pH	*
Conductivity (725 μS/cm)	CDM	9.4 μS/cm	*
Cl^- (2.66 mg/L)	IC	*	2.6 %
NO_3^- (6.55 mg/L)	IC	*	2.4 %
SO_4^{2-} (16.49 mg/L)	IC	*	1.4 %
F (0.67 mg/L)	ISE	*	3.6 %

Legend: ET AAS-atomic absorption spectrometry with electrotermic atomization; CDM-conductivity meter; IC – ion chromatography; ISE – ion selective electrode. Methods are used for water examination in Czech geological survey.

Additional possibility how to get information about method precision from routine analytical work, is from the analysis of duplicates rather then from repeatedly reanalysed QC samples. Analysis of duplicates suit best for matrix samples. From the results of duplicate analysis standard deviation (5) and relative standard deviation (6) are computed as (Uncertainty and traceability, 2001)

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_{i1} - x_{i2})^2}{2n}} \qquad (5)$$

$$RSD \, (\%) = \sqrt{\frac{\sum_{i=1}^{n} (x_{i1} - x_{i2} / \bar{x}_i)^2}{2n}} * 100\% \qquad (6)$$

n is number of pairs, x_{i1}, x_{i2} the first and the second sample determination, $\bar{x}_i$ arithmetic mean of duplicates.

(3)

(4)

As a rule, the analysis of matrix samples gives results with worse precision. A good example of this effect is the conductivity measurement in rainfall water. The ionic strength of these samples is very small, which corresponds to the conductivity lower than 50 mS/cm. During the conductivity measurement, interfering effects, non removable by an operator, counteract. In table 5 the measurement results of these extremely low concentrated samples of 15 pairs of rainfall waters are presented.

Mean samples conductivity 29.4 mS/cm is an arithmetic mean of data in column 4. Standard deviation 1.4 mS/cm was computed after formula (5), relative standard deviation 7.1 % using formula (6).

For comparison: Conductivity remeasurements of QC sample (synthetically prepared from potassium chloride by company Alfa Aesar, molarity of KCl 0.005 $mol.dm^{3-}$) established mean value 725 mS/cm, s = 9.4 mS/cm, RSD = 1.3%. Sample matrix is a real cause of the larger variation of conductivity data in the rainfall samples therefore.

Table 4: Precision details of standard methods corresponding to the methods used in Czech geological survey for water analysis

Standard method	Element/standard analytical method	Sample	s/RSD (%)
ČSN EN ISO 5961	Cd – 0.91 µL / ET AAS	Waste water	RSD: 4.2-8.5 %
ČSN ISO 10 523	pH/range 3-10 pH / glass electrode	Drinking water	s: 0.01-0.05 pH
ČSN EN 27 888	Conductivity – 420 µS/cm / CDM	Natural water	s: 2.23 µS/cm
ČSN EN ISO 10304-1	Cl^- – 11.04 mg/L /IC NO_3^- – 5.37 mg/L /IC SO_4^{2-} – 20.02 mg/L /IC	Surface water Drinking water Synthetic water	RSD: 2.0 % RSD: 2.1 % RSD: 2.0 %
ČSN ISO 10 359-1	F^- – 0.531 mg/L / ISE	Synthetic water	RSD: 2.2 %

Table 5: The conductivity measurement (duplicates) in rainfall water. Unit: µS/cm.

n	x_{i1}	x_{i2}	Arithmetic mean	$\lvert x_{i1}-x_{i2}\rvert$
1	69.4	73.2	71.3	3.8
2	23.8	22.6	23.2	1.2
3	50.5	49.2	49.85	1.3
4	30.7	30.3	30.5	0.4
5	27.5	27.2	27.35	0.3
6	40.8	42.4	41.6	1.6
7	21.3	20.6	20.95	0.7
8	31.1	31.2	31.15	0.1
9	27.1	27.9	27.5	0.8
10	32.1	30.3	31.2	1.8
11	21.3	15.9	18.6	5.4
12	14.3	15.0	14.65	0.7
13	6.0	7.5	6.75	1.5
14	31.0	31.6	31.3	0.6
15	15.0	14.6	14.8	0.4

Summary

Permanent monitoring of precision and trueness practised on QC samples or certified reference materials, makes laboratory possible to obtain high degree of confidence and reliability in routine measurements. As a consequence of this finding, when carriyng out routine measurements, only single determination satisfies.

The size of precision and a difference from a true value of a CRM or a QC sample are parameters that decide about measurement accuracy. Both are inherent to measurement procedure in a full working range. For practical reasons it is desirable to determine them in separate experiments. Knowledge of both contributions to method accuracy is important and necessary in view of a laboratory and its clients, too.

The assessment steps applied in the procedures of this contribution, reflect final treatment of the results from reanalysed QC samples and CRMs. The steps chosen should be regarded as possible ones for correct method validation.

References

Standard Methods for the Examination of Water and Waste Water. Ed. by L.S.Clesceri, A.E.Greenberg, A.Eaton. 20th Edition, Apha, USA, 1998.

Uncertainty and Traceability of the Results from Spectroscopic Methods. Primary course texts. Spectroscopic Society of J. M. Marci, Prague 2001. P.85.

Slovak Geol. Mag., 9, 2 – 3(2003,) 161 – 162

Fractionation analysis – SPE Study Application

JAROSLAV TOMKO, ERIKA KRAKOVSKÁ and DAGMAR REMETEIOVÁ

Department of Chemistry, Faculty of Metallurgy, Technical University Košice, Letná 9, SK – 04200 Košice,
Jaro.Tomko@tuke.sk

Abstract. The toxicity of metal elements, their mobility in the environment and ability to accumulate in living and nonliving systems nearly relate with their chemical forms. Information about their total concentration provides only a little information about their potential risk. In final period in the field of environmental science is collecting great respect at chemical speciation, which arise from requisites to determine concentration especially species characterized with big toxicity and mobility in the environment. Fractionation is process of classification of an analyte or group of analytes from a certain sample according to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties. We have study the efficiency of Cu, Pb, Cd and Zn extraction in dependence on column type and conditioning style. By application both type columns with decreasing concentration of elements in model solutions the extraction efficiency growth. Maximum extraction efficiency was achieved at element concentration in model solution = 100 ppm, another decreasing concentration makes efficiency invariable. Advanced extraction efficiency was achieved by using columns type Merck.

Key words: fractionation, solid phase extraction (SPE)

Introduction

The concept of using an adsorbent material to extract trace organic compounds from an aqueous sample was developed in the 1980s, and its application has been extensively reviewed (Dressler, 1979, Poole at al., 1983). Sorbents are now used to extract organic compounds from various matrices including water, air and event soil. A sorbent with a strong affinity towards organic compounds will retain and concentrate those compounds from a very diluted aqueous or gaseous sample. Many sorbents are specifically suited for the extraction of different groups of organic compounds with various degrees of selectivity. One widely used sorbent technique is solid phase extraction (SPE). The first step of SPE is to pass a liquid matrix through a plastic cartridge or flat membrane containing

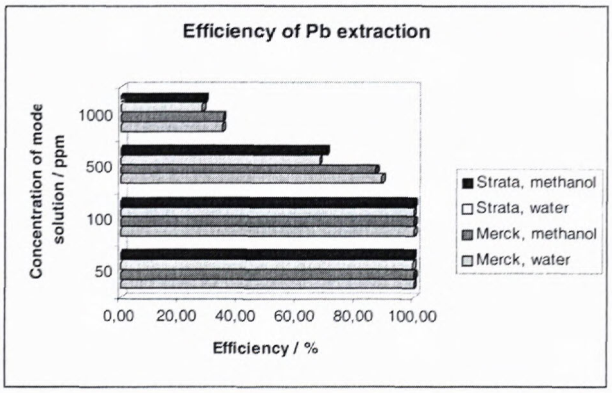


Fig. 2: The efficiency of Pb extraction in dependence on column type and conditioning style.

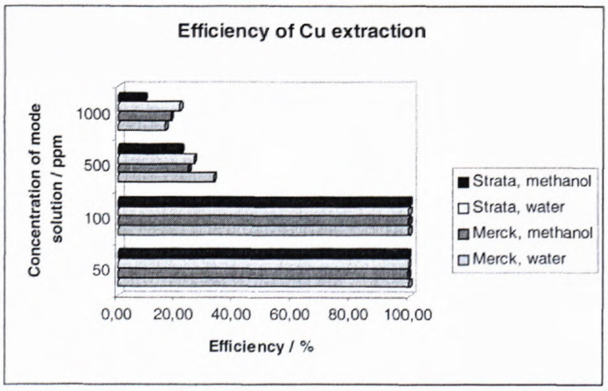


Fig. 1: The efficiency of Cu extraction in dependence on column type and conditioning style.

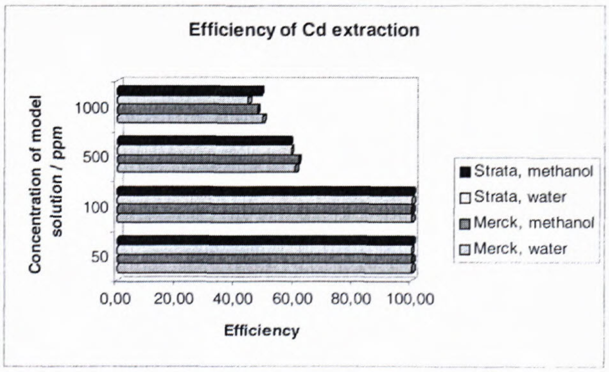


Fig. 3: The efficiency of Cd extraction in dependence on column type and conditioning style.

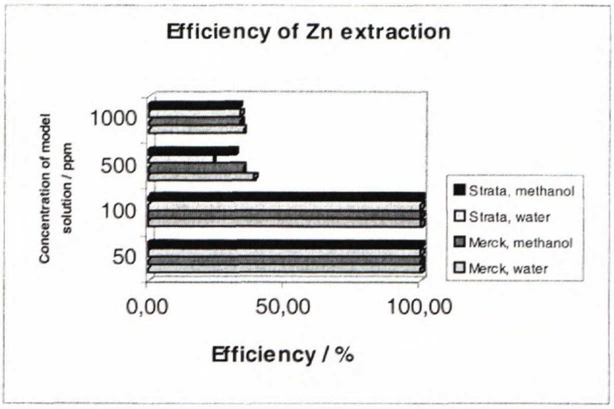


Fig. 4: The efficiency of Zn extraction in dependence on column type and conditioning style.

sorbent dispersed on a particulate support to extract analytes together with interfering compounds (Hagen at al., 1990). Usually, a selective solvent is used to remove interferences first, and then another solvent is chosen to wash out target analytes. SPE has a number of attractive features compared to traditional solvent extraction. SPE is simple, inexpensive, and uses relatively little solvent (Pawliszyn, 1997).

Experimental

Model solutions relevant metallic cations were prepared from hydrate their nitrates cleanness p.a. by melting in 2 times redistilled water. Volume of model solutions was whenever 100 ml. On preconcentration they were employed column Merck LiChrolut SCX 500 mg and Strata SCX 500 mg with volume 3 ml. Columns were conditioning by two ways. By 2 times redistilled water with pH = 5,09 and by mixture of methanol and 2 times redistilled water in the ratio of 1:1 with pH = 6,59. Model solutions were preconcentrated behind tension cut-down at 20 kPa by water air pump. Time of preconcentration was about 45 min. The determination of analytes was carried out with flame atomic absorption spectrometer, the Varian model A-20 plus equipped with deuterium lamp for background correction and air/acetylene flame.

Results and discussion

By application both type columns with decreasing concentration of elements in model solutions the extraction efficiency growth. Maximum extraction efficiency was achieved at element concentration in model solution = 100 ppm, another decreasing concentration makes efficiency invariable. Advanced extraction efficiency was achieved by using columns type Merck.

References

Dressler, M.: J. Chromatogr. **165**, 167 (1979).

Poole, C. F. & Schuette, S. A.: J. High Resolut. Chromatogr. **6**, 526 (1983).

Hagen, D., Markell, C., Schmitt, G. & Blevins, D.: Anal. Chim. Acta **236**, 157 (1990).

Pawliszyn, J.: Solid phase microextraction: theory and practise, Wiley-VCH, Inc, New York, 1997, ISBN: 0-471-19034-9.

Slovak Geol. Mag.,9, 2 – 3(2003), 163 – 166

Toxic Elements in Anthropogeneous Sediments of the Banská Štiavnica/Hodruša Ore District - a Bioavailability Study

KAROL MARSINA[1], DANIELA MACKOVYCH[2], JARMILA NOVÁKOVÁ[2] and HENRIETA ŠOLTÝSOVÁ[2]

[1]Geological Survey of Slovak Republic, Bratislava,
[2]Geological Survey of Slovak Republic – Geoanalytical Laboratories Spišská Nová Ves

Abstract. A bioavailability study was done in the historical Banská Štiavnica/Hodruša epithermal vein precious and base metal ore district on anthropogeneous sediment samples taken from selected sites (tailing ponds, dumps, streams, alluvial plain). 5-step sequential extraction technique was applied to determine the bioavailability of Ag, As, Ba, Bi, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Zn and Cd in 11 samples. Bond of principal and associated ore elements on the studied mineral fractions (1. water soluble, 2. ion-exchangeable and carbonate, 3. reduceable – Fe-Mn oxides, 4. sulphide and organic, 5. non soluble) and relative bioavailability was specified. According to the total and extractable contents of studied elements the association of risk elements was set for the Banská Štiavnica/Hodruša area: Pb, Zn, Cu, Ag, Mn ± Cd.

Key words: anthropogeneous sediments, historical ore district, bioavailability of toxic elements, sequential extraction.

Introduction

Historical ore districts throughout the world are often affected by the activities connected with ore mining, processing and smelting. Highly anomalous total concentrations of potentially toxic elements – major and minor ore constituents – are present in the weathered rocks, soil and sediments. However, strongly enhanced total metal contents do not necessarily endanger the environment, if they are not bioavailable (e.g. sulphide minerals encapsulated in quartz or other chemically inert minerals).

Bioavailability is the proportion of total metals, that are available for incorporation into biota (bioaccumulation – du Bray et al., 1995).

In order to estimate potential risk elements association, a bioavailability study on anthropogeneous sediments of the Banská Štiavnica/Hodruša ore district was done (Marsina et al., 2001) in the frame of the project „Metallogenic evaluation of the Slovak republic" (Lexa, 1998).

The study area

Banská Štiavnica precious and base metal ore district is one of the largest in the Carpathian arc. It is situated in the central zone of the biggest andesite stratovolcano in the whole Carpatho-Pannonian area (diameter almost 50 km), including a caldera (20 km in diameter), resurgent horst and an extensive subvolcanic intrusive complex. Extensive and long living hydrothermal systems gave rise to one of the richest mining districts in Europe. There are about 120 veins at the area of 100 km^2 bearing low sulphidation epithermal precious and base metal mineralisation. Quartz veins are up to several km long, with carbonates and K-feldspars as gangue minerals and predominantly sulphides – chalcopyrite, galena, sphalerite, pyrite (minor sulphosalts) – as ore.

Banská Štiavnica area is well known for its historical mining activities which have begun more than two thousands years ago by Celtic people. Mining spectacularly flourished in the 18th century. An estimate of the total output of mines based on mining archive data stands at 80 tons of gold and 4 000 tons of silver. Base metal production (mainly sulphides) dominated during the 20th century from deeper parts of veins. Roughly 70 000 t of Zn, 55 000 t of Pb and 8 000 t of Cu was produced (Lexa et al., 1999).

Methodology

In the first stage 16 samples of anthropogeneous sediments from selected sites (tailing ponds, dumps, streams, alluvial plain) were taken and analysed for total contents of 23 elements and compounds in the Geoanalytical laboratories of the Geological Survey of Slovak republic – Spišská Nová Ves by AAS – atomic absorption spectrometry, ICP - AES - inductively coupled plasma-atomic emission spectrometry, XRF – X-ray fluorescence spectrometry, high-temperature oxidation, gravimetry and volumetry. The fraction <0,125 mm of stream and alluvial plain sediments was analysed. In the case of tailing pond sediments and weathered material from dumps, the whole sample analysis was done.

In the second stage 5-step sequential extraction technique after Tessier et al. (1979), modified by Fiedler et. al. (1994) was used to determine the bioavailability of Ag, As, Ba, Bi, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Zn and Cd in 11 anomalous samples.

Sequential extraction techniques (speciations) help to explain the physicochemical processes of the metal fixation, mobility and transport. There are two meanings of the speciation:

1. It indicates a procedure, which distinguishes specific elemental form (monoatomic / molecular) or confi-

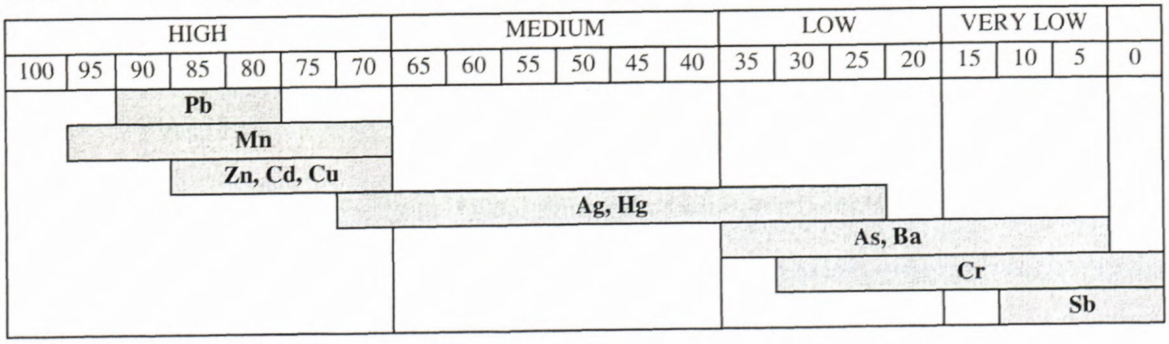
Table 1. Association of risk element contents with studied mineral fractions

		ELEMENT CONTENTS IN FRACTIONS (mg.kg^{-1})								
SAMPLE	**FRACTION**	**Ag**	**As**	**Cd**	**Cr**	**Cu**	**Mn**	**Pb**	**Sb**	**Zn**
1	*1*	-0.5	0.4	-0.5	-1	-1	43	3	-0.1	4
	2	-0.5	-0.1	**3.1**	-1	28	**3 557**	2	-0.1	**443**
	3	**67.2**	**9.6**	**4.6**	-1	**80**	**13 190**	**735**	0.8	**589**
	4	1.3	0.9	0.6	-1	28	265	24	-0.1	157
	5	**24.2**	**67.9**	0.5	**17**	**42**	*0 ?*	73	**19.2**	355
2	*1*	-0.5	-0.1	-0.5	-1	-1	18	3	-0.1	4
	2	-0.5	-0.1	**13.9**	3	136	**6 826**	**900**	-0.1	**2 204**
	3	**2**	2	3	8	81	**2 054**	**616**	0.3	595
	4	1.1	3.5	**16**	2	**1 134**	299	77	-0.1	**3 088**
	5	**4.9**	**22.7**	8.9	**22**	**391**	**2 513**	273	**12.4**	**1 247**
3	*1*	-0.5	-0.1	-0.5	-1	-1	6	4	-0.1	2
	2	-0.5	-0.1	**10.9**	-1	98	**4 192**	**943**	-0.1	**1 544**
	3	**1.5**	1.4	4	4	63	**1 192**	**816**	0.3	784
	4	0.7	2	**14.8**	-1	**753**	171	190	-0.1	**2 678**
	5	**2.6**	**16.4**	7.8	**15**	**237**	839	262	**11.7**	**1 130**
4	*1*	-0.5	0.2	-0.5	-1	-1	45	-2	0.4	12
	2	-0.5	-0.1	3.8	-1	-1	614	-2	-0.1	132
	3	-0.5	-0.1	**60**	**20**	-1	**90 240**	9	3.6	**19 200**
	4	-0.5	5.4	5.7	**26**	**122**	1 865	**116**	1.2	3 042
	5	-0.5	**145**	0.8	**20**	45	2 406	42	**54.8**	4 864
5	*1*	-0.5	0.1	-0.5	-1	5	56	13	-0.1	45
	2	-0.5	-0.1	**1.5**	-1	79	245	**439**	-0.1	**160**
	3	**10.8**	6.2	0.7	-1	**134**	**1 619**	**1 564**	1.1	**300**
	4	1.2	0.3	-0.5	-1	58	92	94	-0.1	121
	5	**6**	**47.9**	0.4	**29**	**174**	**898**	**1 020**	**16.7**	**229**
6	*1*	-0.5	-0.1	-0.5	-1	5	20	33	-0.5	16
	2	-0.5	0.1	14.4	-1	221	**868**	**4 470**	0.6	2 484
	3	**12.7**	4.5	13.7	-1	761	**675**	**8 630**	0.9	2 518
	4	0.5	2.4	**41.9**	-1	**11 260**	72	2 476	-0.1	**8 660**
	5	**38.6**	**55.5**	**50.9**	**13**	**7 967**	355	**7 577**	**12.3**	**10 260**

Table 2. Association of risk elements with studied mineral fractions:

1. Water soluble fraction:	None
2. Ion-exchangeable and carbonate fraction	**Mn, Pb, Zn, Cd** (Cu)
3. Reduceable fraction (metals associated with Fe-Mn oxides)	**Ag, Mn, Pb, Zn, Bi** (Cu, Cd, As)
4. Sulphide and organic fraction	**Cu, Zn Cd** (Ag, Pb, As, Bi)
5. Non soluble fraction (metals fixed in crystalline lattices)	**Sb, Cr**

Table 3. Bioavailability of risk elements (%)



guration of the element. Distinguished forms represent various chemical individuals (ions, complexes, organometallic compounds etc.)

2. It determines individual elemental forms differing in physicochemical conditions as solubility and extractibility by various solvents. Sum of the element contents extracted in single solvents represent the total content of the element in the sample.

5-step sequential extraction technique after Tessier et al. (1979), modified by Fiedler et. al. (1994) was applied in our study. Following elemental forms/fractions were determined and solvents used:

1. ***water soluble fraction*** – elements predominantly in form of inorganic salts.

distilled water

2. ***ion-exchangeable and carbonate fraction*** – elements mainly adsorbed on inorganic salts and carbonates, released into the water, if neutral conditions change into slightly acid conditions.

0,11 M acetic acid

3. ***reduceable fraction*** - metals associated with Fe-Mn oxides, which are thermodynamically unstable and release elements into the water by the redox potential changes.

0,1 M hydroxylamine hydrochloride

4. ***organic and sulphide fraction*** – elements bound in organic matter and sulphides. They are released into the water as a consequence of the organic matter oxidation and degradation / decomposition of the sulphides by the changing physicochemical conditions.

8,8 M hydrogen peroxide
1M ammonium acetate

5. ***non soluble fraction*** - elements fixed in crystalline lattices of primary and secondary minerals

mixture of HNO_3, HF and $HClO_3$

Certified reference material of the stream sediment CRM 601 was used for the quality control testing by comparing measured and certified values. The above material was prepared by the European commission for reference material (BCR).

Discussion of the results

The results of the bioavailability study are discussed on the basis of 6 samples representing various contamination sources and their pathways. Association of risk element contents with studied mineral fractions is shown in Table 1.

Sample 1: sediment from tailing pond „Suchý tajch“ with material from earlier precious metal ore processing with the highly anomalous contents of Ag, Mn and anomalous content of Pb and Zn, associated with fractions *3 (Fe-Mn oxides)* and 2 (carbonates). Sulphides do not play an important role in this type of sediments.

Sample 2, 3: sediments from tailing ponds „Lintich“ and „7 žien“ with material from later base metal ore processing with the highly anomalous contents of Cu, Cd, Mn, Pb, Zn, associated with fractions *4 (sulphides and organics), 2 (carbonates)* and 3 (Fe-Mn oxides). In the contrary to the sample 1 sulphides are the dominant mineral fraction in these sediments.

Sample 4: stream sediment from outflow of the main dewatering gallery „NOŠ“ with material from the Banska Štiavnica/Hodruša ore district with the highly anomalous contents of As, Cd, Sb, Mn, Zn associated with fractions *3 (Fe-Mn oxides)* and *4 (sulphides and organics).* Several km transport of the material caused dissolving of carbonates and higher contents of Zn Cd, Mn (due to better mobility) compared to Cu, Pb.

Sample 5: alluvial plain sediment from the river Štiavnica watershed which drains the ore district with the highly anomalous contents of Ag, Pb, Cu and anomalous content of Zn, associated with fractions *3 (Fe-Mn oxides),* 2 (carbonates) and 4 (sulphides and organics) represent the „classical “ principal ore element association.

Sample 6: weathered mineralised rock debris from the dump near the „Nová šachta" (New shaft) with ore material from later base metal ore processing with the highly anomalous contents of Ag, Bi (66.8 $mg.kg^{-1}$), Cd, Cu, Pb, Zn and anomalous content of As, associated with fractions *3 (Fe-Mn oxides), 4 (sulphides and organics)* and 2 (carbonates) represent the base metal ore enriched in Cu (copper is characteristic for the deeper parts of the ore veins), Ag and Bi (present in sulphosalts, Kovalenker et al., 1991).

Association of risk elements with studied mineral fractions summarises Table 2, bioavailability of risk elements in the Banská Štiavnica/Hodruša ore district is shown in Table 3.

Conclusion

The results show the variability of the anomalous element distribution in anthropogeneous sediments of the researched area.

According to the total and extractable contents of studied elements the following association of risk elements was set for the Banská Štiavnica/Hodruša area:

Pb, Zn, Cu, Ag, Mn ± Cd

The number of studied samples allowed us to point only on some contamination sources of the ore district. It is obvious, that quantitative risk assessment at the Banská Štiavnica/Hodruša ore district will require additional exact data on bioavailability of the risk elements in various media.

The applied 5-step sequential extraction technique has shown good results and could be recommended for further research.

References

du Bray, E. A., ed., 1995: Preliminary compilation of descriptive geoenvironmental mineral deposit models. Report, US GS, Denver, Colorado.

Fiedler, H.D., Lopez-Sanchez, J.F., Rubio, R., Rauret, G., Quevauviller, P., Ure, A.M. & Muntau, H., 1994: Study of the stability of extractable trace metal contents in a river sediment using sequential extraction. Analyst, 119, 1109-1114.

Kovalenker, V. A., Jeleň, S., Levin, K. A., Naumov, B. V., Prokofiev, V. Y. & Rusinov, V. L., 1991: Mineral asseblages and physicochemical model of the formation of gold-silver-polymetallic mineralization in the deposit Banská Štiavnica (Central Slovakia). Geol. Carpath 42: 291-302.

Lexa, J., 1998: Metallogenetic evaluation of the Slovak republic. Scientific project, Geological Survey of Slovak Republic. 27 p. (in Slovak).

Lexa, J., Štohl, J. & Konečný, V., 1999: The Banská Štiavnica ore district: relationship between metallogenetic processes and the geological evolution of a stratovolcano. Mineralium Deposita 34, 639-654.

Marsina, K., Cicmanová, S. & Mackovych, D., 2001: Evaluation of the risk elements species in the mineralised geochemical samples of the various media from the Spišsko-gemerské rudohorie ore Mts. and Banská Štiavnica/Hodruša ore district. Open-File report, Geological Survey of Slovak Republic. 28 p. (in Slovak).

Tessier, A., Campbell, P., G., C. & Bisson, M., 1979: Sequential extraction procedure for the speciation of particulate metals Anal. Chem., 51, 844-851.

Slovac Geol. Mag., 9, 2 – 3(2003), 167 – 170

Quality of Some East-Slovakian Lake Sediments

SILVIA RUŽIČKOVÁ and MIKULÁŠ MATHERNY

Department of Chemistry, Fakulty of Metallurgy, Technical University of Košice, Letná 9, 042 00 Košice,
Slovak Republic, e-mail: Silvia.Ruzickova@tuke.sk, Mikulas.Matherny@tuke.sk

Abstract. Lake sediments were obtained down the axis of reservoirs "Bukovec" and "Domaša" namely from the inflow of feeding lapse till to the outlet. The thermogravimetric analyse (TG) and differencial thermal analyse (DTA) dependences at actual temperature, which slope was mainly linear, were observed. The mass loss in the some definite temperature ranges was regarded in the TG curves. The exothermic maxima and the endothermic minima in the DTA curves we could distinguish. The exothermic maxima were caused wholly by burning of organic parts of studied sediments.

Key words: lake sediments, mineralogy of sediments, thermogravimetry, differential thermal analysis

Introduction

The water reservoirs "Bukovec" and "Domaša" are the typical so-called flow lakes. The water sources, streams and small rivers input on the northern entry end. This flush soil substrates from hanging wall and then form lake sediments. The phase composition of these sediments is considerably monotonous and homogenous along the lake axis. Sediment is made of 70 % of fine-grained quartz, 7-20 % of mica like clay minerals, and considerably variable and inhomogeneous organic part (Hucko & Šumná, 2000). These are mainly non-polar extractable organic matters.

Water and hydroxyl ions in mineral components (Konta, 1952; Matherny, 2002) of flow lake sediments features considerably different forms of appearance (Fig. 1). In principle, this occur is divided into two groups. These are the chemical-bonded water and physical-bonded water, as well. The transition between these two forms is possible but highly complicated. On the other hand, osmosis and adsorption play an important role in this process. The strongest bond of the chemical-bonded water is mediated via the hydroxyl anions. This bond is released at high temperatures (650 – 850 ^{0}C) and crystal structure of water is destroyed during this process. At the considerably lower temperatures (150 – 450 ^{0}C) the crystal and hygroscopically (adsorbed) water, which is bonded in interplanar areas of crystal structures, is loosen. The hygroscopic, adhesive water, is loosen at the lowest temperatures (100 – 135 ^{0}C).

Decomposition temperature of carbonates is different; it starts nearly 850 ^{0}C and terminates nearly 1050 ^{0}C. Quartz is characterized by very compactness structure. Hence, quartz does not contain water neither hydroxyl ions. Merely, the shift between α and β quartz modifications manifest a weak endothermic maximum (Makenzie, 1957).

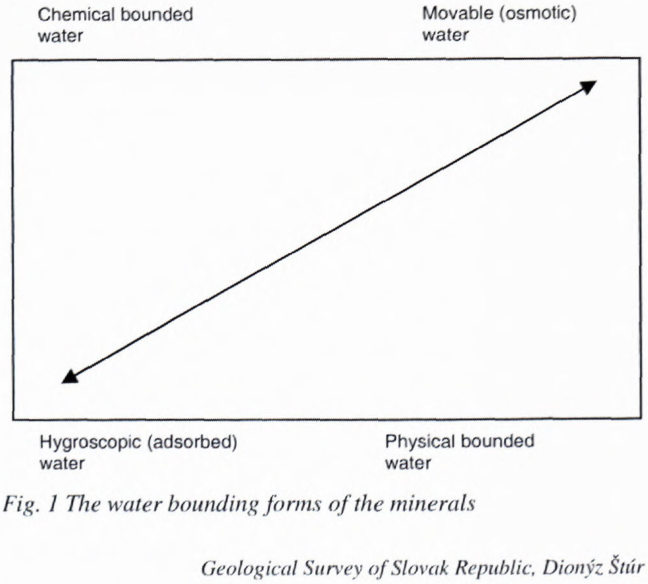


Fig. 1 The water bounding forms of the minerals

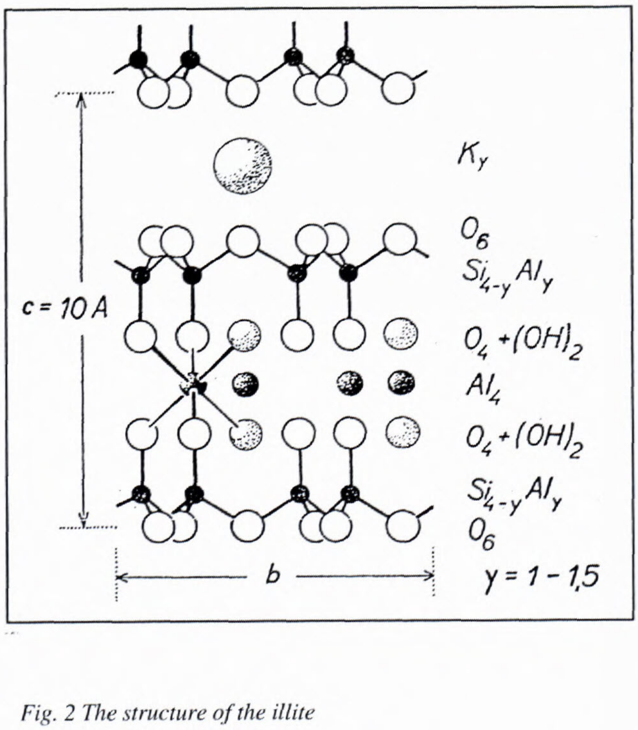


Fig. 2 The structure of the illite

Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava 2003 ISSN 1335-096X

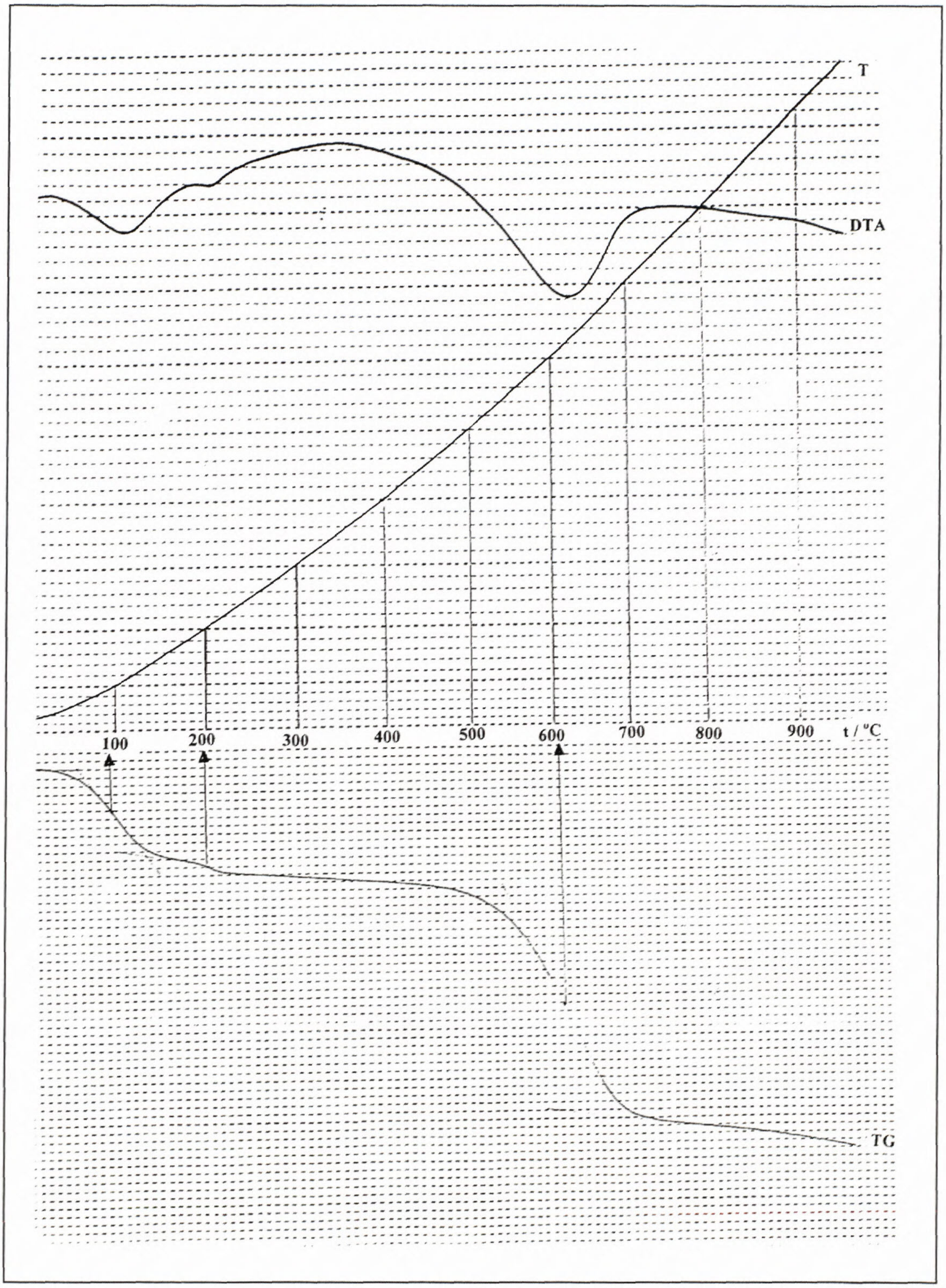


Fig. 3: The T, TG, and DTA curves of the isolated illite minerals.

Another frequent constituents of lake sediments are clay micas. These originate via weathering of acid and intermediate igneous rocks (Betechtin, 1955). These are humus constituents (Nary-Szabo, 1965) and are products of muscovite hydrolysis in association with montmorillonite and kaolinite. The clay micas are transported into water reservoars by rainfalls from the areas above the water structure. The epitome of the clay micas is mineral illite (Kodera et al., 1977). The illite structure illustrates Fig. 2. It is three-layer mineral type with non-expanded structure (so-called mixed structure). Potassium positions are substituted by water molecules and these molecules releases at low temperatures during thermo-chemical reactions. On the other hand, oxygen subrogating hydro-

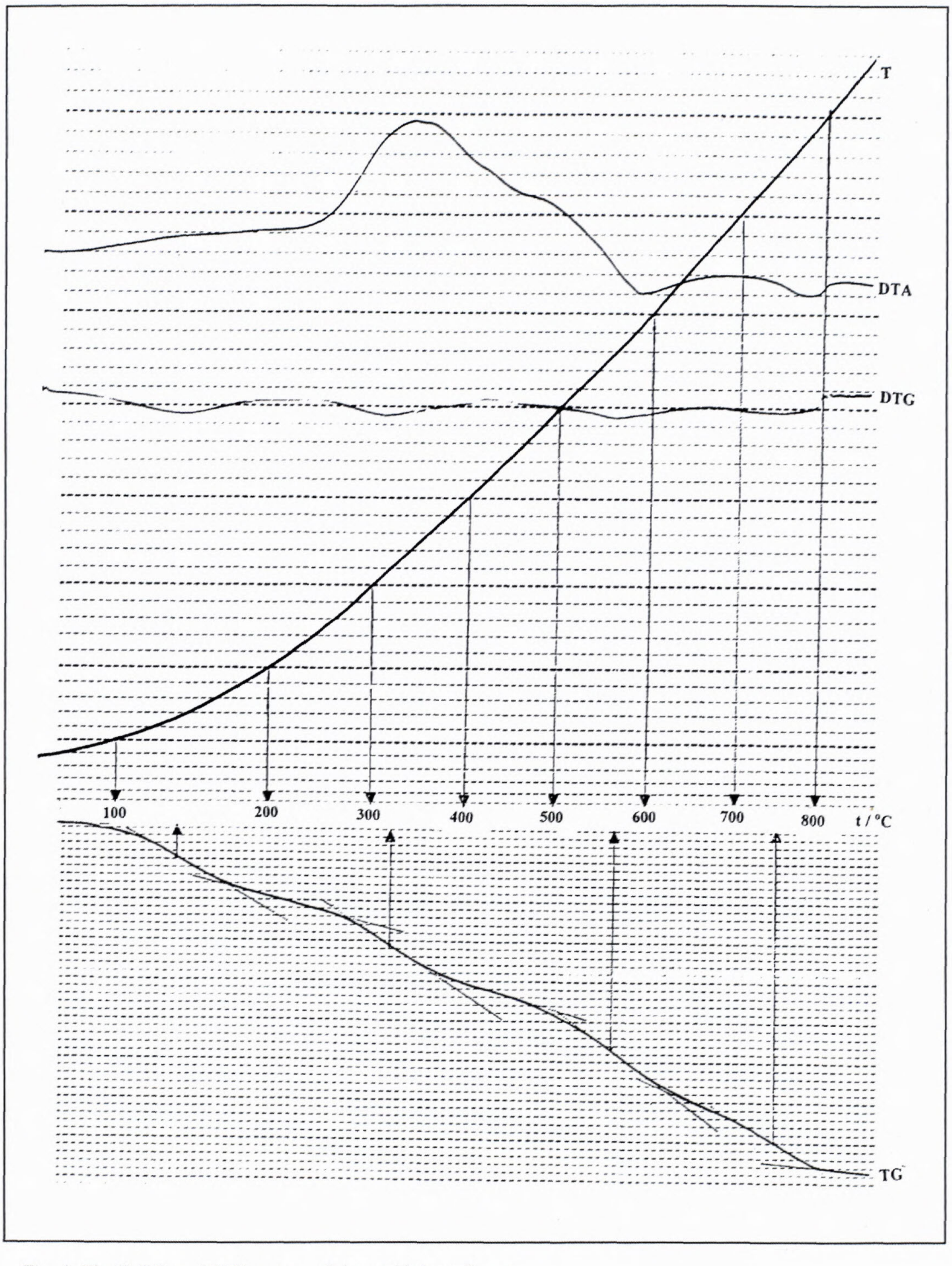


Fig. 4: The T, TG, and DTA curves of the real lake sediment

xyl ions releases over thermal frontier 420°C in the SiO_4 tetraeders (Konta, 1957; Slavík et al., 1956). These endothermic responses of lake sediments containing clay mica overlaps with exothermic responses of organic components. The temperature interval of this response is from 220 °C to 500 °C. Considering the loss of sample during the combustion process, these processes seem like a loss of mass in the thermo gravimetric curves. In the interest of water identification in the lake deposits minerals, the samples were subjected to thermo chemical analysis.

Experimental part

Samples were subjected to thermo-chemical analysis on Derivatographe MON instrument and data were recorded either by photography or by MON recorder. The measurement was performed in the temperature interval from 20 °C to 950 °C. Thermogravimetric, temperature increasement, and differential thermic analyze records were scored. To determine the presence of illite, TGA and DTA records were performed by means of settling method of pure illite (Fig. 3). It is evident from a record that dehydration of illite takes place in three stages. The first stage represents a leakage of physical bounded water with adsorption character from 45 ^{0}C to 140 ^{0}C. The residue of strongly bounded water leaks out at temperature between 150 ^{0}C and 220 ^{0}C. This water substitute particularly K^+ ions and occurs among SiO_4 tetraeder layers. The third stage of dehydration is associated with absolute destruction of illite structure (OH^- ions release) and occurs from 510 ^{0}C to 700 ^{0}C. The first inflection point is found at 95 ^{0}C, the second flex is at 605 ^{0}C.

Discussion

The samples come from the fresh water reservoir Bukovec and from south-northern direction of the ewage basin Domaša. As it can be seen above, TGA and DTA records of particular samples of lake sediments differ from the illite record. The lake sediment samples also showed an exothermic maximum of thermic destruction of organic portion of the lake sediments. Thus, the structure destruction is associated with a leak of products of thermic decomposition (Fig. 4). The thermic decomposition of organic share begins already near temperature 180 ^{0}C and stops at 525 ^{0}C. The inflection point of the process is found at 325 ^{0}C. The record quits by endothermic minimum of reduction of Fe-oxides at 745 ^{0}C.

The values of TG and DTA curves of lake sediments from the water basins Bukovec and Domaša are similar to each other. The significant clay constituent remains illite in sediments from Bukovec and Domaša. Sediments from Bukovec contain approximately constant amount of organic share in dry matter (circa 2 %). On the other hand, sediments from Domaša are characterized by significantly higher fluctuation of the organic share (circa 4 % - 6 %). This fact is quite comprehensive because of vaster Domaša's hanging wall and intense agricultural activities. This activity requires continual application of agrochemicals that are flushed by rainfall to Domaša basin. Some part of these chemicals is water insolubile and is adsorbed by surface-active components as clay; and so chemicals are anchored in lake sediments.

Conclusion

Finally, it can be stated that lake sediments from both Bukovec and Domaša basins contain a mass of flint that is dominant component, next clayey mica, and organic share. The content of carbonates is weak and atypical. Thermic analyze showed that illite is a typical clayey constituent of the lake sediments. The presence of the organic share was confirmed by exothermic maximum on the DTA curves. This exothermic process complicates emission atomic determination of the minor and trace elements of these sediments.

References

Betechtin, A. G., 1955: Mineralogia. SVTL, Bratislava, p. 598.

Hucko, P. & Šumná, J., 2000: Private communication. Closing report of the Reserch Institute of the water resource. Bratislava.

Koděra, M., Ďurovič, S., Masár, I., 1977: Slovenské názvy minerálov. Mineralia Slovaca, 9, 1-81.

Konta, J., 1952: Voda v nerastech. Sborník ÚUG, Praha, p. 241.

Konta, J., 1957: Jílové mineraly Československa. ČSAV, Praha.

Mackenzie, R. C., 1952: The differential thermal investigation of clays. Mineralogical Soc., London, p. 171.

Matherny, M., 2002: Vplyv vlhkosti na chemizmus stavebných materiálov. Zborník konferencie "Intenzifikácia ochrany stavebných objektov". SPU, Nitra.

Náray-Szabó, I., 1965: Kristálykémia.Akadémiai Kiadó, Budapest, p. 420.

Slavík, F., Novák, J., Pacák, O., 1956: Mineralogie. ČSAV, Praha, p. 316.

Slovak Geol. Mag., 9, 2 – 3(2003), 171 – 172.

Monitoring of Persistent Organic Pollutants in Environment of Slovak Republic

DANKA ŠALGOVIČOVÁ, ZUZANA SASKOVÁ, ANGELA SVĚTLÍKOVÁ and SLÁVKA KRÍŽOVÁ

Výskumný ústav potravinársky (Food Research Institute), Priemyselná 4, 824 75 Bratislava

Abstract. In the article monitoring results of POPs in selected parts of environment are presented. Ten of twelve POPs were monitored in the Slovak Republic. The monitoring was provided by workers of the Ministry of Agriculture SR, the Ministry of Health SR and Ministry of Environment SR.

Apparently, obtained results from monitoring of food and biota do not reveal a discontented situation. There is not even a documentary negative trend, but this problem must be taken into consideration in order to minimize penetration of POPs into food chain and consecutively into consumers diet.

Key words: perzistent organic pollutants, monitoring, soil, food, feed, water

Perzistent Organic Pollutants (POPs) are chemical substances that remain intact in the environment for long periods. They become widely distributed geographically and accumulate in the tissue of plants and living organism. However they are toxic to humans and wildlife their persistence enables them to be transported by air, water to remote regions where they have never been used. Chemicals as dioxins, polychlorinated biphenyls and organochlorinated pesticides can be ranged into this group.

It was observed an interesting coherence among exposure to POPs and a wide range of effects on human health including cancers, skin desease, nerve and mental disturbance, exchange of immune system, reproductional disturbance, etc. These substances act as a greatly negative in human tissues. Above mentioned compounds can be cummulated in human milk and post-leak into the sucklings bodies. Even in minimal concentrations they have significant impact on the development of brain.

Although POPs include a wide range of chemicals, much of the research is directed toward 12 chemicals that include 3 main groups (by International Programme of Chemical Safety ,1995):

- **Pesticides -** Aldrin, Chlordan, DDT, Dieldrin, Endrin, Heptachlor, Mirex and Toxafen
- **Industrial chemicals -** Hexachlorbenzene and PCBs
- **Unwanted by-products of various industrial processes -** Dioxins and Furans [1].

Ten of twelve POPs were monitored in the Slovak Republic. Following table of monitored POPs in several parts of environment was worked out on the basis of the studied analyses.

The main aim of POPs monitoring was to give in detail analyse of their actual situation in all parts of environment and human population and to prepare a proposal for their future monitoring.

The specific aim was to summary the condition of existing information on monitoring of POPs in environment and human population of Slovakia and to evaluate the revelance of this subject to Environmental Monitoring in the Slovak Republic.

Following sections dealing with POPs monitoring at present:

- Environmental section
- Health section
- Agricultural section

Monitoring of POPs within the framework of the environmental department is engaded by the Geological Survey of Slovak Republic and Conservation and Slovak Hydrometerological Institute. These organizations are able to carry out monitoring of POPs in surface water, waste water, sediments and water living being creatures.

The POPs are monitored at health department by the Institute of Preventive and Clinical Medicine, State Health Institute of Slovak Republic and eighteen Health Care Institutions. These organizations are dealing with monitoring of foods, air, water, sediments, human milk and human materials.

Monitoring of POPs at agricultural department is performed by Central Control and Testing Agriculture Institute, Research Institute of Water Management, State Veterinary and Food Administration, Institute of Soil Science and Conservation, the Slovak Water Managment Enterprise and its organizations (The Hron River Basin, The Vah River Basin, The Danube River Basin, The Bodrog and Hornad River Basin, Hydromelioracie) and the Food Research Institute. The agricultural department ensures monitoring and analysing soil, sediments, water, feeds, water and forest animals and different types of foods.

General 26 organizations were assigned to the monitoring of POPs which provide results of analysed and

Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava 2003 ISSN 1335-096X

Table - Summary processed questionnaire about several commodities

Commodity	Aldrin	Chlordan	DDT	Dieldrin	Endrin	Heptachlor	HCB	Mirex	Toxafen	PCB	Dioxins	Furans
Emissions										**x**	**x**	**x**
Ground-water	x		x	x	x	x	x			x		
Surface-water	x		x	x	x	x	x	**x**	**x**	x		
Irrigation water	x		x	x	x	x	x			x		
Feed water										x		
Drinking water	x		x	x	x	x	x			x		
Wastewater	x		x	x	x	x	x			x		
Rain water										x		
Recreational water	x		x	x	x		x			x		
Agricultural soil	x		x	x	x	x	x			x		
Anthrophogenic sediments	x		x	x	x	x	x	**x**	**x**	x	**x**	**x**
Wastes		x	x	x	x	x	x			x		
Plant production	x	x	x	x	x	x	x			x		
Animal feeds	x		x	x	x	x	x			x		
Water living being animals			x			x	x			x		
Forest animals and birds			x				x			x		
Animal production	x	x	x	x	x	x	x	**x**	**x**	x		
Human milk			x				x			x	x	x
Human material			x				x			x		
Foods and drinks	x	x	x	x	x	x	x			x		
Another	x	x	x	x	x	x	x			x	x	x

x - Additional initiative monitoring

evaluated contents of aldrin, chlordan, DDT, dieldrin, endrin, heptachlor, HCB, PCB, dioxins and furans.

Average findings of monitored chemicals do not shown values approaching required limits. Only PCBs, aldrin, DDT and HCB were monitored regularly. Others POPs were monitored only occasionally (endrin, dieldrin a heptachlor), or not at all (mirex, toxafen).

POPs in agricultural soil have exhibit a decreasing tendency. Results of point charging soils show high concentration of PCBs only.

Apparently, obtained results from monitoring of food and biota do not reveal a discontented situation. There is not even a documentary negative trend, but this problem must be taken into consideration in order to minimize penetration of POPs into food chain and consecutively into consumers diet [2].

References

Monitoring perzistentných oraganických látok v Slovenskej republike (Technická správa č. 2), Bratislava, Ministerstvo životného prostredia, 2003, 185 s.

Vyhodnotenie národnej legislatívy a inštitucionálnej infraštruktúry vo vzťahu k POPs v Slovenskej republike (Technická správa č. 1), Bratislava, Ministerstvo životného prostredia, 2002, 71 s.

Slovak Geol. Mag., 9, 2 – 3(2003), 173 – 176

PCBs and Dioxins in Sediments and Surface Waters of the Michalovce Region

JÁN PETRÍK[1], JANA CHOVANCOVÁ[2] and ANTON KOČAN[3]

[1]Slovak Health University, Institute of Preventive and Clinical Medicine,
[2]National Center for Dioxins and Related Compounds,
[3]Limbová 12, 833 03 Bratislava, Slovak Republic

Abstract. 21 sediments (Zemplínska Šírava – water reservoir, Laborec River, Veľká Domaša – water reservoir, Ondava River, Váh River, Nitra River) and 11 samples of surface water (Zemplínska Šírava - reservoir, Morské oko Lake, Vinianske Lake, Laborec River) were analyzed for polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs) and polychlorinated biphenyls (PCBs) including mono-ortho-substituted and planar congeners.

The content of PCDDs/Fs in sediments was determined by the US EPA 1613 method using high-resolution mass spectrometry (HRGC/HRMS). In total, 17 "dioxin" congeners and 12 mono-ortho-substituted and planar toxicologically important PCB congeners were analyzed in the samples collected.

Analysis of PCBs in sediments was done by low-resolution mass spectrometry (modified US EPA 1668) and in surface water samples by the method of gas chromatography with electron capture detection.

Samples were collected from December 2002 to May 2003. The obtained results point to carrying over contamination with PCBs in the Michalovce region.

Key words: sediment, surface water, PCBs, dioxin, PCDD/Fs

Introduction

The environmental fate and behavior of individual PCB congeners are influenced by physical-chemical properties, mainly by volatility, water solubility and lipophilicity. Less chlorinated congeners have higher vapor pressure and are more water-soluble than higher chlorinated ones. The congeners with higher number of chlorines are more lipophilic. These differences influence composition of individual congeners in different environmental matrices. PCBs present in surface water are adsorbed on particulates, accumulate in sediments and subsequently concentrate in tissues of water organisms. Due to their possible mobilization from sediments, accumulation in the food chain, and finally in the human body they represent a potential risk for human health (Salizzato et al., 1998). Major sources of environmental contamination with PCBs in the Slovak Republic are PCB production in eastern Slovakia during the period of 1959-1984 and PCB use. In total, 21,482 tones of PCB formulations were produced there. It has been declared that 11,613 t were used inside former Czechoslovakia chiefly as heat exchanger fluids, capacitor and transformer dielectric fluids, and paint additives. It is estimated that about 1,600 tones of PCB wastes were generated during the production. PCBs are positively detected in all environmental compartments of Slovakia such as air, surface water, sediments, soil, foodstuffs and human biological tissues as well (Kočan et al., 1998).

Sediments from the area of former PCB production in Slovakia show high values even 14 years after its ceasing – up to 4.1 mg.kg^{-1} (avg. 0.3 mg.kg^{-1}) (Kočan et al., 1999, Petrík et al., 2001). Sediment PCB levels from water bodies from the other areas of Slovakia range between 0.01-2.8 mg.kg^{-1}. Samples with high content of PCBs come mainly from the areas of high industrial activities. The measu-rements conducted in 1983-2001 document that 24 % of surface water samples (SHMÚ, 2003) contained more than 10 ng PCBs/L - recommended maximum concentration.

Material and methods

The sediment samples for this study were collected using UWITEC sampler and/or manually with a scoop. The water samples were collected according to STN ISO 5667-4,6. Collection of sediments was performed from October to December 2002 and water samples in May 2003. All samples were processed immediately after delivery to the laboratory.

Determination of PCDD/F/dioxin-like PCBs in sediments (HRGC/HRMS)

The sediment was dried at max. 50 °C, grinded and sieved. The fraction below 2 MM I.D. was used for next processing. Approximately 5 grams of homogenized sample was extracted in Soxhlet apparatus after spiking with a known amount $^{13}C_{12}$ labeled extract standards. The toluene extract was after concentration cleaned-up by a modified silica column. The final eluate was fractionated using basic alumina and subsequently by an activated carbon column. After evaporation to dryness the sample was reconstituted with known volume of the syringe standard and analyzed by HRGC/HRMS in MID (Multi Ion Detection) mode. Individual PCDD/Fs and dioxin-like PCBs were identified by comparing GC retention time and ion-abundance ratio of two exact m/z 's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of two exact m/z's. Quantitation was done by isotope dilution mass spectrometry technique using calibration standards containing $^{13}C_{12}$ labeled and unlabelled congeners according to USEPA 1613 and USEPA 1668 methods.

Determination of other PCB congeners in sediments (HRGC/LRMS)

The samples were prepared as written above. Homogenized samples were extracted with n-hexane/diethyl ether mixture. The clean-up procedure was performed on an H_2SO_4/silica column. Quantification was carried out by high-resolution gas chromatography (HRGC) with low-resolution mass spectrometry (LRMS) in a single ion-monitoring (SIM) mode using USEPA 1668 method. More details are given in (Petrík et al., 2001, Kočan et al., 1994).

Determination of other than dioxin-like PCBs in surface water samples (HRGC/ECD)

Surface water samples spiked with clean-up standard were filtered. Combined extracts from the aqueous and solid portions were cleaned-up on a florisil-silica/H_2SO_4 column. The eluates were allowed to evaporate to dryness and subsequently were reconstituted with the syringe standard solution. HRGC/ECD conditions and method of quantitation are given in detail in (Kočan et al., 1999, Krupčík et al., 1992).

Results and discussion

The results of „dioxins" and PCBs in sediments and surface water samples from different sampling sites of Slovakia are presented. Just PCB analyses were performed in water samples.

It is obvious from the results of surface water samples (Table 1) that the contamination of waterways is not on very high level even though the values from Zemplínska Šírava and the river of Laborec are still slightly above the recommended limit (10 $ng.L^{-1}$) for surface water in the Slovak Republic (Regulation 491, 2002). We found out almost the same values as were determined in the previous study (Kočan et al., 1999).

As it can be seen from Table 1 the highest concentrations were determined in Zemplínska Šírava (sampling sites inflow and outflow canals). These samples were taken below the Chemko Co. effluent canal merges the Laborec River. Laborec is the main source, which the reservoir is filled from. Sampling sites ZŠ Paľkov and Kamenec located on the eastern side of the reservoir without direct influence of Laborec waters present a little bit lower level of PCB pollution. Similarly, rather low values were determined in the forest lakes Morské oko and Vinianské Lake. Both these ecosystems have no direct (through the river of Laborec and/or ZŠ) connection to contaminated industrial effluent canal of Chemko Co. Low PCBs were also found in Laborec above the former producer (Chemko Co.). Atmospheric deposition is the most probable contributor of PCBs to these waters.

Table 1 Concentration of PCBs in surface water samples.

	Kočan et al., 1999	**This study**
	$ng.L^{-1}$	
Zempl. Šírrava (Biela h.)	20	20.7
Zempl. Šírrava (Medvedia h.)	19	25.3
Zempl. Šírrava (Kusínn)	14	-
Zempl. Šírrava (Palkov)	-	15.3
Zempl. Šírrava (Kamenec)	-	14.4
Zempl. Šírrava (Hôrka)	-	24.6
Zempl. Šírrava (inflow canal)	55	43.3
Zempl. Šírrava (outflow canal)	17	29.3
Laborec (above Chemko co.)	13	7.0
Laborec (below Chemko Co.)	68	-
Čierna voda Channel	16	-
Senné fish ponds	10	-
WWT plant (outflow canal)	64	-
Effluent canal (Chemko Co.)	1950	-
Merged canal (WWT-plant+Chemko Co.)	1338	-
Domaša	7	-
Ondava	9	-
Olšavka	10	-
Morské oko (inflow)	-	4.0
Morské oko (outflow)	-	5.4
Vinianské Lake	-	8.1

Sediments analyzed within this study were sampled from different water bodies around Slovakia. By assumption the highest values of PCBs and „dioxins" were determined in sediments from the industrial – effluent canal from the factory of Chemko Co.). The increased values were observed also in sediments from the river of Laborec and Zemplínska Šírava as well. The other watercourses (Nitra and Váh) show PCB values on the background levels measured in the previous study (Kočan et al., 1999). Comparison of PCB data measured in Zemplínska Šírava sediments collected in 1997/98 (Kočan et al., 1999) and 2002 (this study) is shown in Fig. 1.

The results of PCDD/Fs show very low contamination in the Laborec and Ondava rivers and in Veľká Domaša reservoir. The moderate contamination was observed in Zemplínska Šírava. These data are comparable with published data (Schramm et al., 1997, Bruckmeier et al., 1997, Fattore et al., 1997, Rappe et al., 1997, Buckland et al., 1997) for background and/or not industrially contaminated areas.

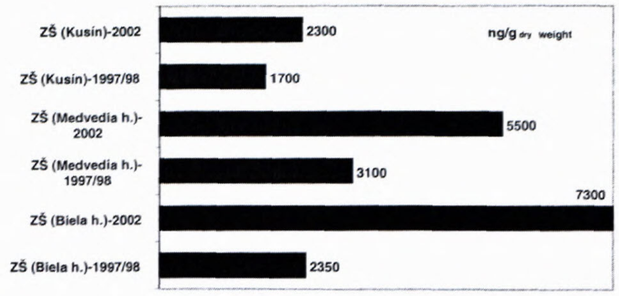


Figure 1 PCB content in sediments from Zemplínska Šírava.

None of the sediments had quantifiable levels of 2,3,7,8-TCDD. Except OCDD and 1,2,3,4,6,7,8-HpCDD none of other CDD congeners were determined almost in all sediments. The main contributors of the „dioxin" toxicity in the samples from the area of Chemko Co. are shifted from PCDD to PCDF as a consequence of PCB pollution. It can be seen from the Figure 2 that even in low contaminated sediment samples TEQs from PCBs comprise considerable contribution to the total TEQ values.

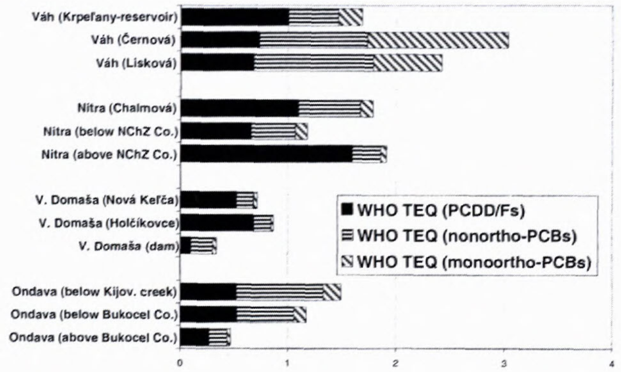


Figure 2 Contribution of PCDD/Fs and dioxin-like PCBs to the total TEQ values in selected sediments.

Conclusions

It is obvious from the comparison of water samples from Zemplínska Šírava and other Slovak water bodies collected in 1997/98 and 2003 that just samples taken in surroundings of the former PCB producer reach values above recommended value for surface waters. Although the PCB production was ceased almost 20 yrs. ago the industrial effluent canal from the factory (see *Table 1*) is the most probable source of contamination with PCBs in this area. PCBs accumulated in sediments are just slowly mobilized into water. This situation will last probably till the remediation starts.

PCDD/Fs levels in sediments represent the first data in Slovakia. The PCDD/F ratio reflects the source of possible contamination. TEQ values of the samples collected near the Chemko Co. effluent canal consist mainly of PCDFs. The other samples with low PCDD/F concentrations show approximately similar contribution of PCDDs and PCDFs.

Table 2 PCBs and „dioxin" concentrations in sediments.

	PCDD/Fs	**0-ortho-PCBs**	**1-ortho PCBs**	**PCBs**
	[WHO-TEQ, pg/g$_{D.W.}$]			[ng/g$_{D.W.}$]
Ondava (above Bukocel Co.)	0.27	0.17	0.032	19
Ondava (below Bukocel Co.)	0.53	0.53	0.11	27
Ondava (below Kijov. Creek)	0.52	0.81	0.16	40
Effluent canal (below Chemko Co.)	56	233	113	108611
Effluent canal (below WWT plant)	341	1963	1236	733210
Effluent canal (road Strážske-Michalovce)	586	1992	1039	566726
Laborec (Voľa)	0.23	11	6	1377
Laborec (Nacina Ves)	0.098	6.8	3.6	967
Laborec (Petrovce)	261	712	431	98445
Zemplínska Šírava (Biela hora)	20	53	20	7308
Zemplínska Šírava (Medvedia hora)	21	74	22	5511
Zemplínska Šírava (Kusín)	13	27	7.6	2277
V. Domaša (dam)	0.1	0.2	0.039	36
V. Domaša (Holčíkovce)	0.68	0.16	0.029	16
V. Domaša (Nová Kelča)	0.52	0.16	0.038	11
Nitra (above NChZ Co.)	1.6	0.26	0.05	22
Nitra (below NChZ Co.)	0.66	0.41	0.11	133
Nitra (Chalmová)	1.1	0.57	0.11	74
Váh (Lisková)	0.68	1.1	0.64	116
Váh (Černová)	0.73	1	1.3	204
Váh (Krpeľany reservoir)	1	0.46	0.23	45

References

Buckland, S. J., Ellis, H. K., Salter, R. T. (1997): Baseline levels of PCDDs, PCDFs, PCBs and organochlorine pesticides in New Zealand rivers and estuaries, Organohalogen Compounds, 32, 12-17.

Bruckmeier, B. F. A., Juettner, I., Schramm, K-W., Winkler, R., Steinberg, Ch. E. W., Kettrup, A. (1997): PCBs and PCDD/Fs in lake sediments of Grosser Arbersee, Bavarian forest, south Germany, Environmental Pollution, 95, 19-25.

Fattore, E., Benfenati, E., Mariani, G., Fanelli, R. (1997): Patterns and Sources of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Sediments from the Venice Lagoon, Italy, Environ. Sci. Technol., 31, 1777-1784.

Kočan, A., Petrík, J., Chovancová, J., Drobná, B., (1994): Method for the group separation of non-ortho-, mono-ortho- and multi-ortho-substituted polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans using activated carbon chromatography. J. Chromatography, 665, 139-153.

Kočan, A., Drobná, B., Chovancová, J., Kočan, J., Petrík, J., Szabová, E., (1998): Burden of the environment and human population in the area contaminated with PCBs. Interim report, Project No. 105/98-2.4., IPCM Bratislava, November, 113 pp, (*in Slovak*).

Kočan, A., Petrík, J., Drobná, B., Chovancová, J., Jursa, S., Pavúk, M., Kovrižnych, J., Langer, P., Bohov, P., Tajtáková, M., Suchánek, P., (1999): Burden of the environment and human population in the area contaminated with PCBs. Final report, Project No. 105/98-2.4., IPCM Bratislava, February, 217pp, (*in Slovak*).

Petrík, J., Kočan, A., Jursa, S, Drobná, B., Chovancová, J., Marián Pavúk (2001): Polychlorinated biphenyls in sediments in Eastern Slovakia, Fresenius Environ. Bull. 10, 375-380.

Rappe, C., Andersson, R., Cooper, K., Fiedler, H., Lau, C., Bonner, M., Howell, F. (1997): PCDDs and PCDFs in lake sediment cores from Southern Mississippi, USA, Organohalogen Compounds, 32, 18-23.

Salizzato, M., Bertato, V., Pavoni, V, Ghirardini, A. V., Ghetti, P. F., (1998): Sensitivity limits and EC50 values of the *Vibrio Fischeri* test for organic micropollutants in natural and spiked extracts from sediments, Environ. Toxicol. Chem. 17, 655-661.

SHMÚ (2003): Initial assistance to the Slovak Republic to meet its obligations under the Stockholm Convention on Persistent Organic Pollutants (POPs). Technical report No. 2 (Draft), Part 1, Project No. SLO/01/G31, SHMÚ Bratislava, April, (*in Slovak*).

Regulation 491 (2002): Regulation of the Government of the Slovak Republic from July 17, 2002 (Statute book No. 491/2002).

Schramm, K-W., Winkler, R., Casper, P., Kettrup, A. (1997): PCDD/F in recent and historical sediment layers of lake Stechlin, Germany, Wat. Res., 31, 1525-1531.

Slovak Geol. Mag., 9, 2 – 3(2003),177 – 179

The Environmental Risks in Regard to Production and Collection of Selected Medicinal Plants Species

IVAN ŠALAMON

Department of Ecology, Faculty of Humanities and Natural Science, Presov University in Presov 1,
17th November St., SK-081 16 Presov, *salamon@fhpv.unipo.sk*

Abstract. The important and complex environment problems for very longtime are a pollution of fair, soil and water by xenobiotics. There are anorganic (heavy metals) and organic components (pesticide residues), which are not the natural origin or their quantity in ecosystem can be effected from unhealthy to toxic. The largest catastrophe in history of civil using of nuclear energy was in Chernobyl, Ukraine, in April 26th, 1986. The radioactivity has effected to vegetation in the Slovak Republic even if the Chernobyl crash was many years ago. The medical quality and effect of medicinal plants are depended on the conditions of environment, which is influenced direct to their grow on the place of an occurrence and cultivation.

Environmental risks (content of heavy metals, pesticide residues and radioactivity) in regard to production and collection of medicinal plants (Chamomile, Calendula, Linden, Mallow, Peppermint) was determined by the analytical methods. In spite of the results, the trace xenobiotic values and radioactivity of medicinal plants were stated. The results were compared by the Slovak Republic legislation. The heavy metal, pesticide residues contents and radioctivity of medicinal plant samples are not higher than the maximum permissible concentration and radiation in regard to the Regulation No. 14/1996 & No. 12/2001 of the Ministry of Healthy Service in Slovak Republic. These raw materials can be accepted on the market with medicinal plants in the world.

Key words: medicinal plants, heavy metals, residue pesticides, radioactivity

Introduction

The important and complex environment problems for very longtime are a pollution of fair, soil and water by xenobiotics. There are anorganic (heavy metals) and organic components (pesticide residues), which are not the natural origin or their quantity in ecosystem can be effected from unhealthy to toxic. The largest catastrophe in history of civil using of nuclear energy was in Chernobyl, Ukraine, in April 26th, 1986. The radioactivity has effected to vegetation in the Slovak Republic even if the Chernobyl crash was many years ago. The medical quality and effect of medicinal plants are depended on the conditions of environment, which is influenced direct to their grow on the place of an occurrence and cultivation. In regard to medicinal plant market, it is very important to determine the hazard values of herb goods to domestic and foreign customers and compare their with the regulation on the highest permissible toxic effects in food, which are notified by the Slovak legislation.

The aim of contribution is determination of heavy metal and pesticide residue contents and radioactivity in selected medicinal plants, which are collected and produced in Slovak Republic during last years.

Material and Methods

The conserve plant parts (flowers and herbs) by drying of Chamomile (*Matricaria recutita* L.), Calendula (*Calendula officinalis* L.), Linden (*Tilia cordata* L.), Mallow (*Malva mauritiana* L.) and Peppermint (*Menta piperita* L.) were used to our measurement. This plant material was originated from a wild plant collection and large-scale cultivation of these medicinal plants in Slovak Republic in years: 2000, 2001 and 2002.

Determination of Heavy Metals

The herbal samples for the heavy metal determination were decomposed by 10 ml HNO_3 and 1 ml H_2O_2 into vessels, which were given in a pressure autoclave. Mineralization was taken place at the temperature 150 ^{0}C during 5 hours. The AAS results for Cd, Pb, Cr, Ni, Cu and Zn were obtained using SHIMADZU, model 660, with Graphite fumace, deuterium background corrector and auto-sampler. Sample volumes were 20 ul. The AAS resutls for Hg were obtained using hydride vapor generation technique SHIMADZU, model HVG-1.

The quantity values of heavy metal and element contents obtained in the single medicinal plants are compared with the highest permissible concentrations according to the Regulation No. 14/1996 from the Ministry of Healthy Service in Slovak Republic.

Determination of Pesticide Residues

The pesticide residues were determined by the GC-method with an application of equipments: type Varian Star, model 3,400, and Varian Star, model 3,800; the detector ECD after plant sample arrange. Identification of

Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava 2003 ISSN 1335-096X

these risky components was made on base of retentive characteristics comparing between them and standard compound. All these chemical analysis were carried out in the Ecological & Veterinary Laboratories in Spisska Nova Ves, Slovakia.

The quantity values of pesticide residues obtained in plant materials are compared with the highest permissible concentrations according to the Regulation No. 14/1996 from the Ministry of Healthy Service in Slovak Republic.

Radioactivity Tests

The conserve plants were used to determination of the mass radio-nuclide activities. The gama-spectrometric determination of selected medicinal plants by the HPGe detector with using of Cesium (^{134}Cs & ^{137}Cs), Americium (^{241}Am), Potassium (^{40}K), Radium (^{226}Ra) and Thorium (^{232}Th) radio nuclides was carried out at the Special State Health Institute, Department of Health Protection against the Radioactivity in Banska Bystrica, Slovakia.

The quantity values of radioactivity obtained in these flower and herbal materials are compared with the highest permissible concentrations according to the Regulation No. 12/2001 from the Ministry of Healthy Service in Slovak Republic.

Results and Discussion

The heavy metals, as one from foot element groups, have a very important ecological significance, which is given their toxicity and accumulation ability. Influence of heavy metals for environment is more expressive their any degradation. The determined heavy metal contents and additional microelements in the medicinal plant drugs (note: substances used as or in medicine) are presented in table 1.

Table 1:Determination of heavy metals and additional microelements quantities in selected medicinal plants.

	Cadmium [Cd]	Lead [Pb]	Mercury [Hg]	Chrome [Cr]	Nickel [Ni]	Cuprum [Cu]	Zinc [Zn]
	[mg.kg^{-1}]						
Chamomile flower drug	0.180	0.315	0.002	0.267	1.67	13.08	12.90
Calendula flower drug	0.078	0.225	0.003	0.154	0.87	15.05	20.89
Linden flower drug	0.095	0.756	0.011	0.360	0.55	10.89	10.21
Mallow flower drug	0.028	0.158	0.002	0.095	1.90	19.02	21.18
Peppermint herbal drug	0.021	0.086	0.005	0.102	1.55	18.77	23.52

Table 2:Results of residue pesticide determination into the medicinal plant drugs.

Residue pesticides [mg.kg^{-1}]	Chamomile flower drug	Calendula flower drug	Linden flower drug	Mallow flower drug	Peppermint herbal drug
aldrine + dieldrine	< 0.0005	< 0.0005	0.0023	0.0020	0.0007
alfa-hexachlorecyclohexane	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
beta-hexachlorecyclohexane	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
delta-hexachlorecyclohexane	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
eldrine aldehyde	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
endrine	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
endrine ketone	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
endosulphane sulphate	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
endosulphane I	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
endosulphane II	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
gama-hexachlorecyclohexane	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
hexachlorebenzene	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
chloreepoxide+heptachlore	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
heptachlore	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
metoxychlore	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
sum DDT	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005

Table 3:The flower and herbal drugs of selected medicinal plants and their radioactivity.

	natural radionuclides			artificial radionuclides		
[Bq.kg^{-1} of plant sample]	^{232}Th	^{226}Ra	^{40}K	^{241}Am	^{137}Cs	^{134}Cs
Chamomile flower drug	< 5.9	< 4.0	44	< 4.7	< 1.7	< 1.8
Calendula flower drug	< 3.5	< 0.5	25	< 1.3	< 0.8	< 0.9
Linden flower drug	< 6.4	< 3.4	365 ± 35	< 4.3	4.4 ± 0.6	< 4.3
Mallow flower drug	< 2.1	< 0.8	10 ± 5	< 2.0	< 0.5	< 0.6
Peppermint herbal drug	< 3.6	< 1.7	330 ± 30	< 2.1	< 0.8	< 0.8

The very unfavourable comparative of heavy metal concentration (Cd and Pb) in medicinal plant rawmaterials, which were obtained from the cultivation in Scotland, Findland and in the Central Europe was published in 1994 (Svoboda & Gough). The medicinal plant drugs from our area (the Central Europe) were contamined by double quantities of Cadmium and Lead concentrations more than another rawmaterials.

The need of better preparations to manage of wide range of the harmful gents (weeds, diseases and pests) of cultivate crops is determined the massive character of the synthetic chemical preparations, which use very often in regard to medicinal plant cultivation. The very problematic question is a metabolism and degradation of pesticides in the single plant species. (Schuphan, Schmidt & Veit, 1990). The present production of the special crops is not possible without direct pesticide application. On the other hand, a control of pesticide residues in individual phases of ontogenetic plant development and into the final product or yield is inevitable (Oravec, Buben, Černaj, Repčák & Hončariv, 1981). Table 2 illustrates the values of determined residue pesticides in the medicinal plant drugs.

Characteristics of mass radio-nuclide activities of ^{232}Th, ^{226}Ra, ^{40}K, ^{241}Am , ^{134}Cs, and ^{137}Cs in Bq.kg^{-1} of plant materials are presented in table 3.

Measures of mass radio-nuclide activities of medicinal plant drugs have not carried out yet; the results are original. It was determined that radioactivity of individual medicinal plant species are dependent on time and exposure in a space. The flowers of Linden are growth in tree height, where their exposure is very high. The radioactivity results of Linden flowers were confirmed this predication.

There are medicinal plants, which exposure on the high places is continued several years. Icelandic Lichen, *Cetraria islandica* /L./Ach., can be a good example. This thallophytic plant is occurred on the rocks in the High and Low Tatras (the Slovak parts of Carpathian Mountains). In regard to radioactivity determination of Icelandic Lichen thallus were gotten at from 350 to 600 Bq.kg^{-1} of ^{134}Cs & ^{137}Cs mass radio-nuclide activities.

Conclusion

Legislation of state in regard to hazardous interactions in environment is connected with human consciousness, control and measurement of chemical, physic-chemical and physical measurement and their influence for biological systems. At present is very important to introduce the Europe environment recommendations.

Environmental risks (content of heavy metals, pesticide residues and radioactivity) in regard to production and collection of medicinal plants (Chamomile, Calendula, Linden, Mallow, Peppermint) was determined by the analytical methods. The results were compared by the Slovak Republic legislation. In spite of the results, the trace xenobiotic values and radioactivity of medicinal plants were stated. These raw materials can be accepted on the market with medicinal plants in the world.

References

Oravec, V., Buben, I., Černaj, P., Repčák, M. & Hončariv, R.: Herbicidal Experiments the Station for Development of Medicinal Plant Large Scale Cultivation. Symposium Novi Sad, 1981, p. 34.

Schuphan, I., Schmidt, B. & Veit, P.: Pesticide Metabolism and Degradation in Plants. In: Gesunde Pflanzen, Vol. 42, 1990, No. 4, s. 276-280.

Svoboda, K. P. & Gough, J. E.: Herb crops in the U. K. – an overview of current trends in production and development. In: Journal of the Science of Food and Agriculture, Vol. 57, 1994, No. 3, pp. 193-202.

Slovak Geol. Mag., 9, 2 – 3 (2003), 181 – 187

Quality of the Atmospherically Dustiness of the City Košice and Surrounding

KATARÍNA UHRINOVÁ, KAROL FLÓRIÁN and MIKULÁŠ MATHERNY

Department of Chemistry, Faculty of Metallurgy, Technical University of Košice
Letná 9, SK-042 00 Košice, Slovakia, e-mail: Katarina.Uhrinova@tuke.sk

Abstract. The atmospherically dustiness has three origins: emissions dustiness, the imissions, dustiness and the last form is the deposited part. The deposited dustiness formed the gravitation dust sediments with the diameter higher as 10 μm. The given particles sediment spontaneously. This part of atmospherically dustiness was in the residential agglomeration of the city Košice patterned during the year periods 2000 till 2002.The dust samples were taken according to the DIN standardized Bergerhoff method. Finally it was necessary to observe not only the total amount of gravitation dust sediments, but also their chemical composition

Firstly was evaluated the changing of the monthly amount of the gravitation dust sediments. Furthermore the evaluation of the experimental results was directed towards to the study of correlations-regressions phenomena between the monthly amount of gravitation dust sediments and the individual element amounts,

As a result can by stated that the most frequented and well-correlated elements with the amount of dust particles are the elements Fe, Mn and Ti. The elements Cu and Zn enter in to the atmosphere from the exhaust of pyrometallurgically factories in the basin of the river Hornad (Rudňany, Krompachy). The concentration of Pb is high and this element enters in the real time in the atmosphere from the exhaust gasses of petrol engines. The rest of trace elements like Co, Cr, Ni, Sn, and V possess a variable character and create the trace elements background of the atmospherically dustiness.

Key words: Atmospherically dustiness, gravitation sediments, statistical evaluation, correlation, regression

Introduction

The atmospherically dustiness from the standpoint of its genesis consist of tree components: the dustiness indicated by the emitted dust of emission point sources, the transported dustiness bounded with the distant imissions, and finally the deposited, spontaneous sediment dust particles (Junge 1962). On the genesis of given dustiness forms beside the source characters, meteorological and geographical parameters the main influence has the idealized particle side (Junge 1962, Malisa & Robinson 19779, Einax et al. 1991). The particles with diameter less as 1 μm not are to able spontaneous sediment generally. On the opposite side the particles with diameter higher as 10 μm sediment always spontaneously. The particles with diameter between 1 to 10 μm sediment only partially and this sedimentation is mainly given by the interaction of their chemical character and meteorological conditions (fog, rain, snow). This phenomenon is called mainly as: washing of the atmosphere. The deposited part of atmospherically dustiness creates the gravitation dust sediments (further only dust). Airborne dust particles are also partially shaped by the anthropogenic activity in the residential agglomerations. That ones elevate the atmospherically toxicity.

The genesis of the predominant elements (C as graphite, SiO_2, Ca, and Mg carbonates), subsidiary elements (Al, Fe, Mn, Ti) and the whole group of different trace elements are very dissimilar. While the surface elements (Al, Ca, Mg, Ti) penetrated in the atmosphere by the erosion of soils, the other common elements (C, Si, Fe, Mn) and the have metal elements come partially from the emissions of industrial activities (Ure & Davidson 1985).

Experimental part

The dust was sampled by the Berghoffer method (VDI/DIN 1996) in glass pots. This pot was during winter period filled by methylalkohol, and in the other year periods only with distillated water. By these additives the powder particles was stabilized. The obtained mixture of rain and solid particles was firstly at 105 °C evaporated and finally at 125 °C dried to the constant weigh. The chief sampling station was situated in the middle part of the city Košice on the top of the main building of Technical University. The auxiliary sampling stations are in the wide surrounding of Košice (Fig. 1): in the middle part of city Prešov (36 km western), and the villages Dargov (31 km eastern), Moldava (29 km western), and Čaňa (20 km southern). The sampling period was restricted on the years 2000, 2001 and 2002 with monthly interval. The amount of the sampled dust is expressed in t km^{-2} $year^{-1}$ units. Opposite the individual elements amount in dust was expressed in kg km^{-2} $year^{-1}$.

In this powder samples was from the group of common and surface elements only the concentrations of Fe, Mn, and Ti determined. The predominant elements (C, Si, Ca, Mg) were not followed because the used analytical method was optimized for the concentration range of subsidiary and trace elements. For the concentration deter-

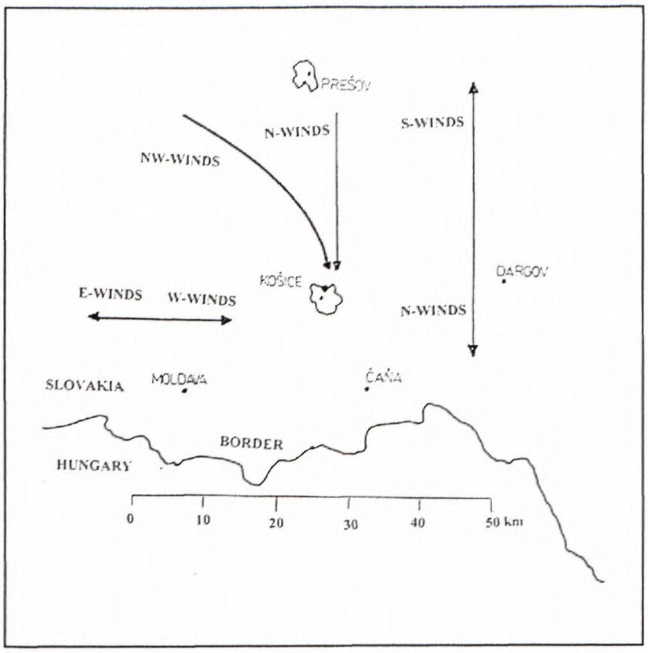


Fig. 1. The sampling stations in East-Slovakia

mination of chosen subsidiary and trace elements (Co, Cr, Cu, Ni, Pb, Sn, V and Zn) was used the optimized method with excitation in DC arc (Flórián et al. 1992). The concentration of the light volatile elements (Ag, Bi, Mo, and Sb), and the high toxic elements (As, Be, Cd, Hg) was not determined because their concentration level was clear low as their analytical limits of detection ($\bar{m}(X)_L \approx 0.02$ ppm). From the environmental standpoint mentioned light volatile and toxic elements in the given region are not typical pollutants. By the statistical evaluation in the attention of outstanding comparability were the "eigenvalues" applied.

Results and Discussion

The complexes exploratory statistical analysis of the data of dust amount was realized with the software QC Expert 2.5 (Kupka 2002). These calculations built mainly on the calculation of arithmetical mean $\bar{m}$, the median $\tilde{m}$, the modus $\hat{m}$ and the half sum m_p values and the testing of the asymmetry, the excess, the homogeneity and normal distribution of experimental values.

The comparisons of the data from the five sampling stations (Tab. 1) confirmed that the amount of the dust is homogenous distributed and this distribution have normal Gausian character. In the Fig. 2 is given the example of the most characteristic early-optimized histogram, the distribution curve and the round-like diagram for the sampling station Čaňa. The conformity the real functions with the theoretical is very high what consideration the above confirms. But the characteristic values for the sampling station Moldava (Fig.3 and Tab. 1) demonstrate the least advantageous example. This consideration demonstrates mostly the different courses of the histograms and the round-like diagrams. The similarity of the computed data for the sampling stations in Košice, Čaňa and Prešov (Fig. 1), which is the direction of the prevailing N → S winds (ca 67 %), is most expressive.

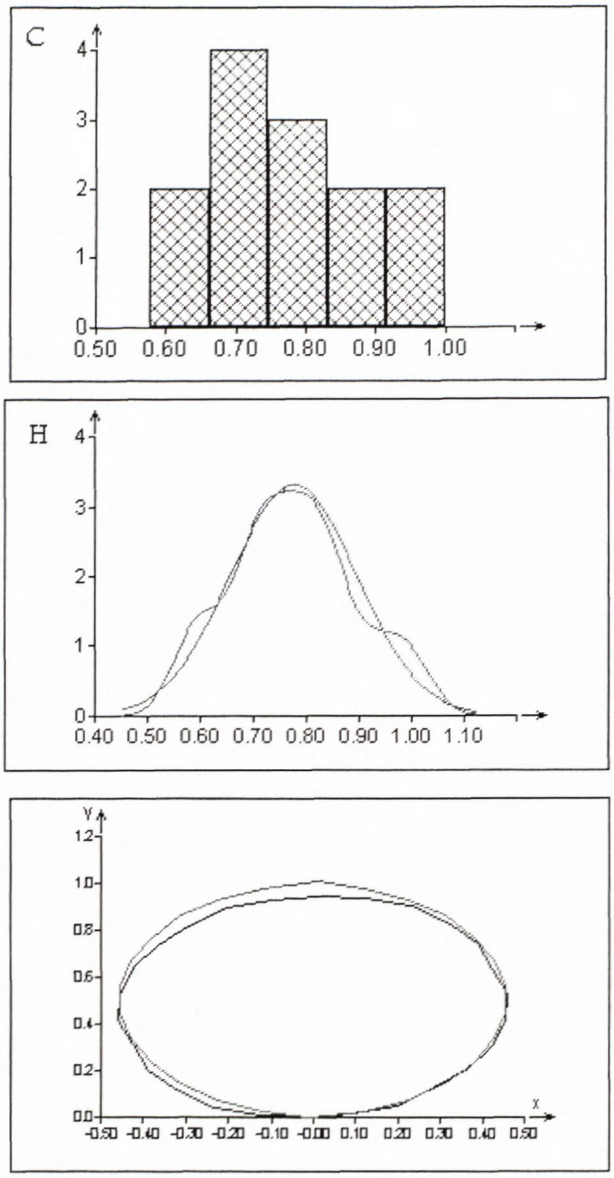


Fig. 2. The histogram, the distribution curve and the round-like diagram of the dust amount in Čaňa, C - multiplicity, H - density

The detailed analysis of the statistical properties of the dust from Košice shoved the following results. The fluctuation of the total amount of gravitation dust sediment in the years from 2000 till 2002 is illustrated in the differential histograms (Fig. 4) of the Δm values. This present the difference between the monthly measured values m_i and the annual arithmetical mean value $\bar{m}$.

$$\Delta m = m_i - \bar{m}$$

It is possible to distinguish two years period in the given histograms. The first period, from November till May of the next year is demonstrated in all observed tree years with marked dustiness maximum. This conclusion confirmed that the meteorological conditions have domi-

Table 1: Evaluated statistical parameters of the dust amounts

Sampling stations	$\overline{m}$	$\tilde{m}$	$\hat{m}$	m_p	***Asymetry***	***Exces***	***Homogenity***	***Normality***
Košice	0.58	0.57	0.55	0.57	akcepted	akcepted	akcepted	akcepted
Čaňa	0.78	0.77	0.76	0.77	akcepted	akcepted	akcepted	akcepted
Prešov	0.63	0.64	0.65	0.64	akcepted	akcepted	akcepted	akcepted
Dargov	0.71	0.71	0.71	0.71	akcepted	akcepted	akcepted	akcepted
Moldava	0.66	0.70	0.77	0.66	not akcepted	akcepted	akcepted	akcepted

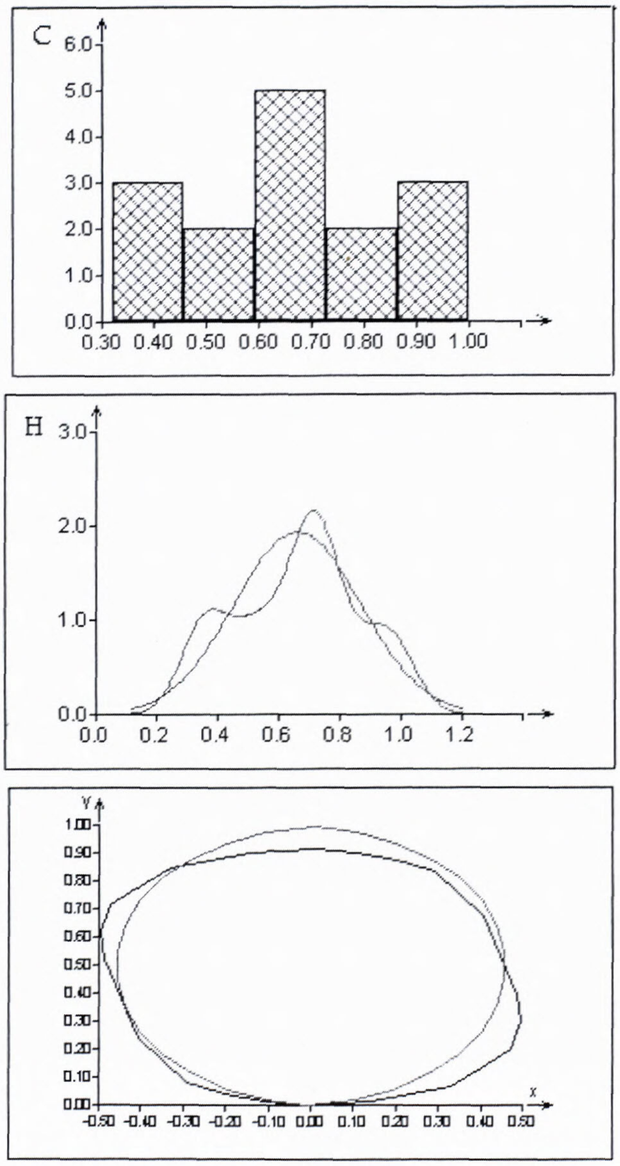


Fig. 3. The histogram, the distribution cure and the round-like diagram of the dust amount in Moldava, C - multiplicity, H - density

nant character in this case. In this period prevailed in all East-Slovakian regions the N and NW winds (67 %). These winds cleans the region from the pollutants because northern from Prešov are nothing expressive pollution sources which contaminated the atmosphere with inorganic products. The second period, from June till October, is in opposites position and it is marked with dustiness maximum. The N and S winds are in equality in this considered period. This winds are contemporary minimal (7 %) and therefore is their influence expressions less. The south part of the East-Slovakia has a lowland character with intensive agricultural activity. The intensive erosion of the soil causes the contamination of the atmosphere with the surface elements (Al, Ca, Mg, Ti). Only one artificial case (2000, August) from the regularity of the diversity of minimal and maximal dustiness was found.

Tab. 2. The values of correlation and regression coefficients

	Correlation coefficients		***Slopes***	
Elements in dust	r_{min}	r_{max}	a_{min}	a_{max}
Fe	0.78	0.91	0.87	1.0
Mn	0.32	0.71	0.33	0.92
Ti	0.17	0.88	0.18	1.0
Zn	0.22	0.78	0.24	0.93
Cu	-0.26	0.16	-0.25	0.23
Pb	-0.07	0.21	-0.08	0.28
Cr	-0.29	0.09	-0.27	0.12

The monthly fluctuations of the individual followed elements are enough different. The limiting values of correlation coefficients and the values of slopes of the counter ellipses, which present the regression lines, are listed in the table 2.

The most similarity of the distribution of Fe amount with the amount of dust is demonstrated in the Fig. 5. The average amount of Mn is about factor 8 to 10 lower. Therefore the monthly differences are also lower and the two different periods are not clear (Fig. 6). The similarity of Ti distribution with the distribution of precipitated dust particles is not so pregnant (Fig. 7). It is necessary to be aware that the geneses of Ti amount have another character as the other subsidiary elements.

The further trace elements have very element specific distribution character. The genesis of Cu (Fig. 8) and Zn (Fig. 9) elements is bounded on the emissions of pyrometallurgical factories in the Hornad river valley. The pollution and therefore also the element distribution of the atmosphere are conditioned by the campaigner character of the metallurgical production. This valley flow in the funnel shaped Košice valley and contaminate irregular the all-residential agglomeration. Lastly the amount of

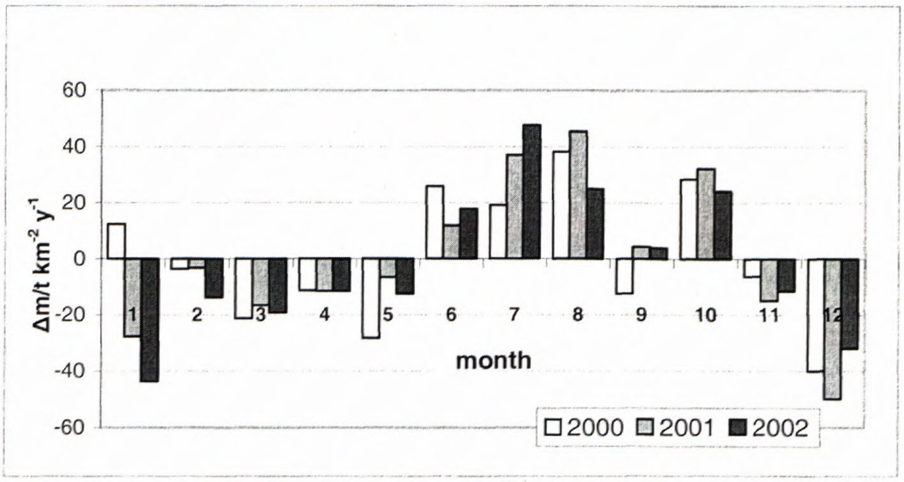


Fig. 4. Monthly swinging of the dust amount in the years 2000 till 2002 in t km^{-2} y^{-1} units. $\overline{m}$ *(2000) = 78.9,* $\overline{m}$ *(2001) = 71.3,* $\overline{m}$ *(2002) = 59.9*

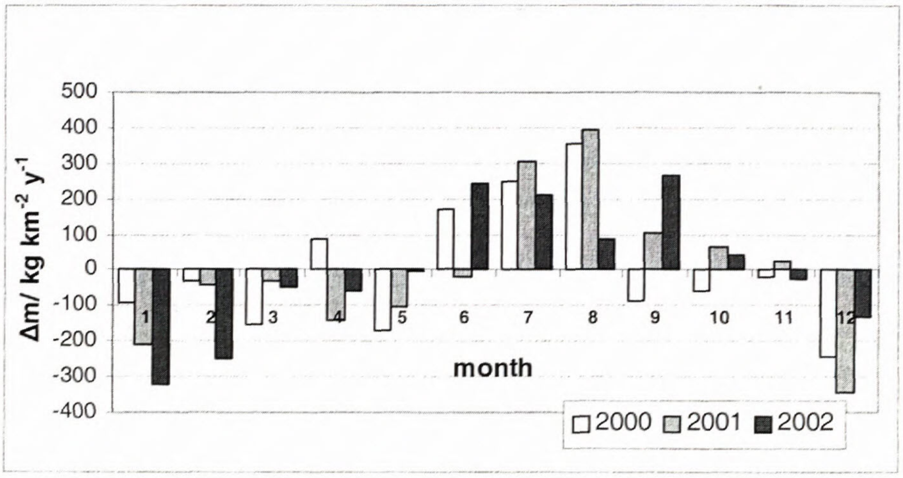


Fig. 5. Monthly swinging the Fe amount of dust in the years 2000 till 2002 in kg km^{-2} y^{-1} units. $\overline{m}$ *(2000) = 417.4,* $\overline{m}$ *(2001) = 424.1,* $\overline{m}$ *(2002) = 362.1*

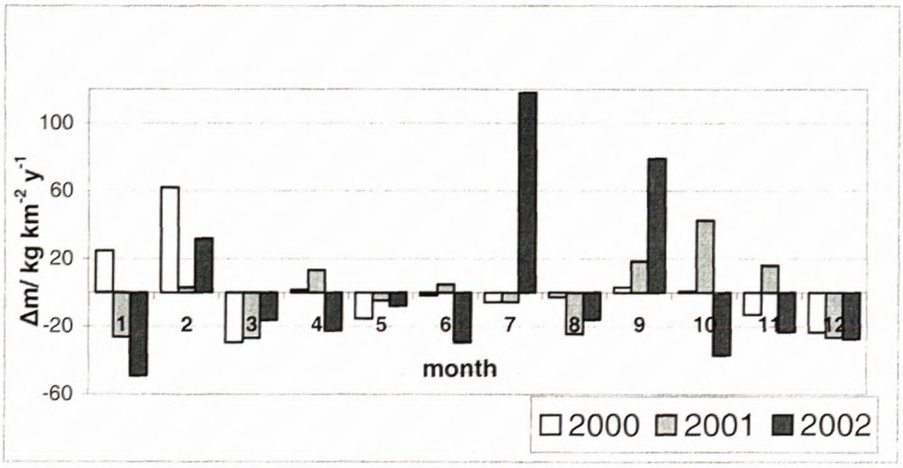


Fig. 6. Monthly swinging the Mn amount of dust in the years 2000 till 2002 in kg km^{-2} y^{-1} units. $\overline{m}$ *(2000) = 51.1,* $\overline{m}$ *(2001) = 42.6,* $\overline{m}$ *(2002) = 54.9*

Cr and the other followed trace elements is low, approximately 1 till 6 kg km^{-2} y^{-1}. The distribution of the amount of Cr (Fig. 10) is without any regularity.

In continuation of the dustiness research, the correlation-regression analysis and the construction of the scatter diagrams was applied were applied. In the first dustiness period the correlation-regression analysis between the Fe amount and the amount of gravitation dust sediment (Fig. 11) shows high correlation (r = 0.91) and also almost ideal regression (w = 0.99). The courses of the confidence limits lines are very narrow to the regression line. The counter diagram was denoted as clear and narrow

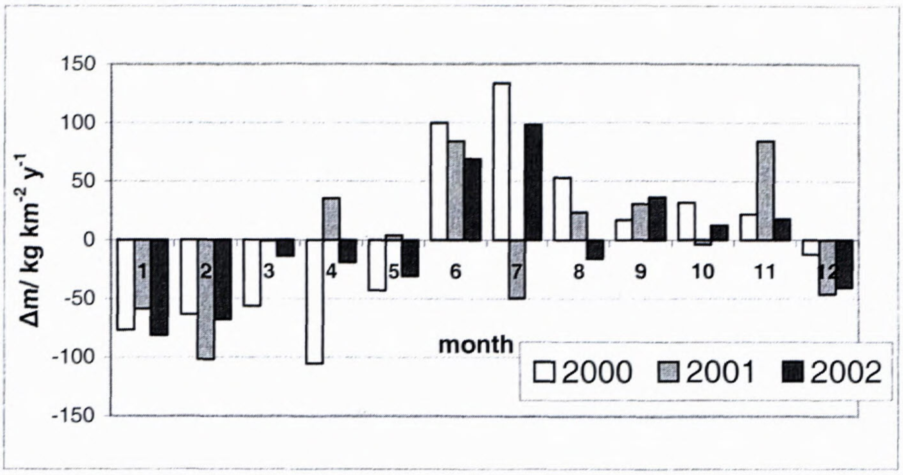


Fig. 7. Monthly swinging the Ti amount of dust in the years 2000 till 2002 in kg km^{-2} y^{-1} units, $\overline{m}$ (2000) = 105.3, $\overline{m}$ (2001) = 101.7, $\overline{m}$ (2002) = 100.0

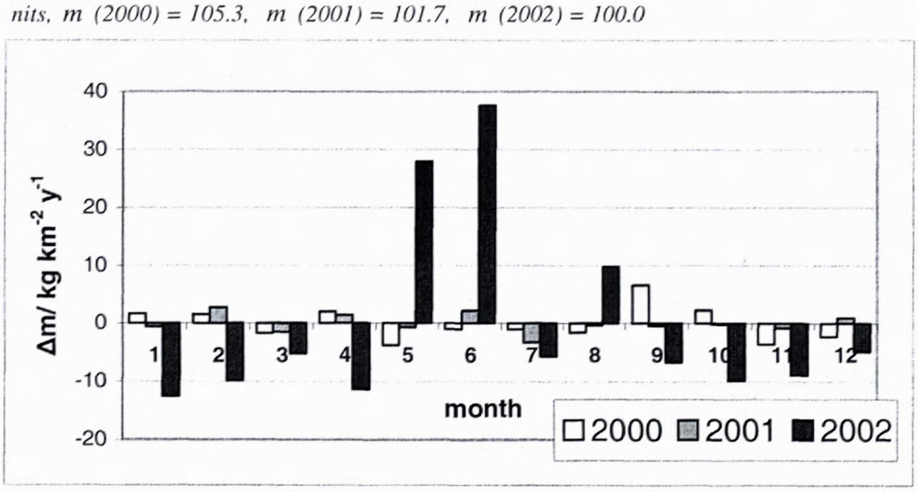


Fig. 8. Monthly swinging the Cu amount of dust in the years 2000 till 2002 in kg km^{-2} y^{-1} units. $\overline{m}$ (2000) = 6.0, $\overline{m}$ (2001) = 4.4, $\overline{m}$ (2002) = 14.0

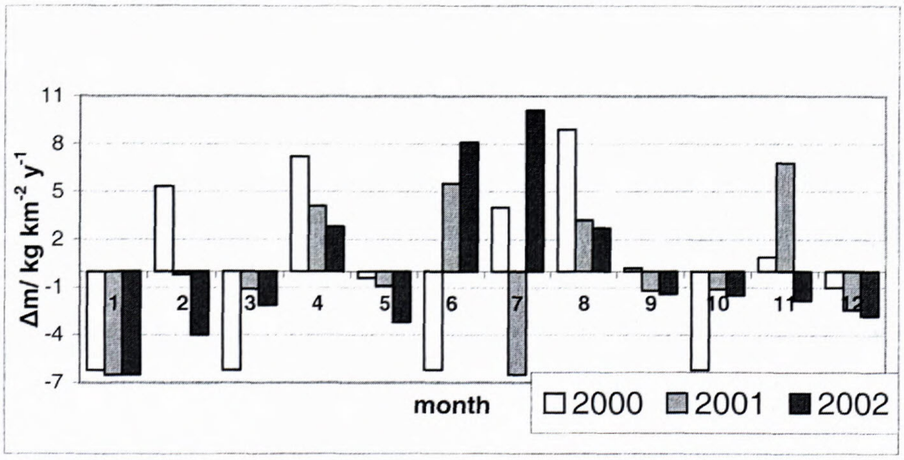


Fig. 9. Monthly swinging the Zn amount of dust in the years 2000 till 2002 in kg km^{-2} y^{-1} units. $\overline{m}$ (2000) = 6.2, $\overline{m}$ (2001) = 6.5, $\overline{m}$ (2002) = 8.2

ellipse. These results confirmed that the genesis of Fe amount direct related with the total dustiness amount. In the second dustiness period under equivalent frequency of N and S winds the correlation expressively fall to the value r = 0.45. This worsen of the correlation was caused by the dilution of the atmosphere with S winds with amount of surface elements and changeable Fe amount. Unequivocal dependence for the Mn and Ti amounts was found. Their correlation coefficients for the years 2000 till 2002 moved for the amount of Mn between the values ⟨0.32, 0.70⟩ and for Ti between ⟨0.17, 0.88⟩. Contemporally was confirmed a lower regression as by the Fe amount. The dependence for the amount of Cr (Fig. 12), which ire presents the clear trace elements, shows that

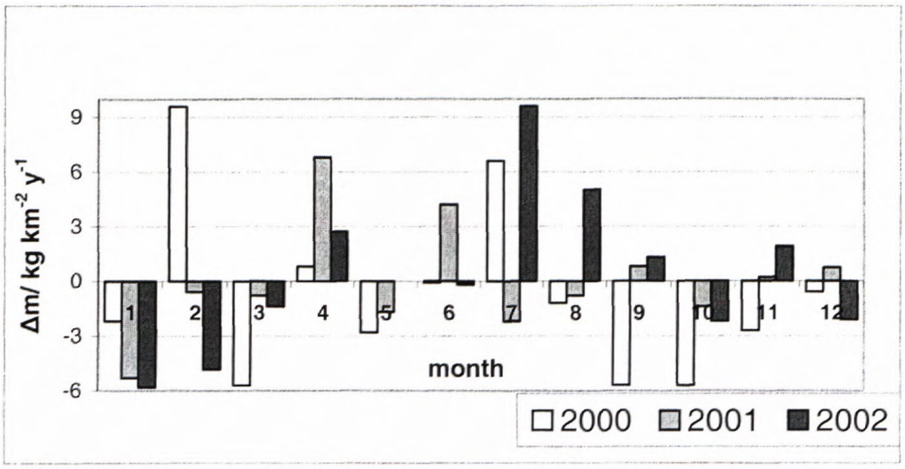


Fig. 10. Monthly swinging the Cr amount of dust in the years 2000 till 2002 in kg km^{-2} y^{-1} units. $\overline{m}$ *(2000) = 5.7,* $\overline{m}$ *(2001) = 5.3,* $\overline{m}$ *(2002) = 7.2*

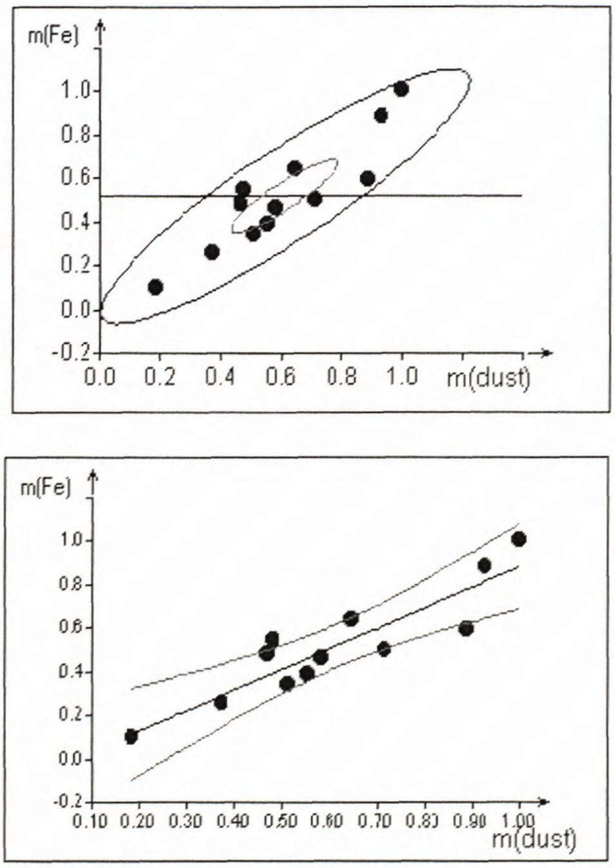


Fig. 11. The scatter diagram and the regression straight line for the Fe / dust amount ratio

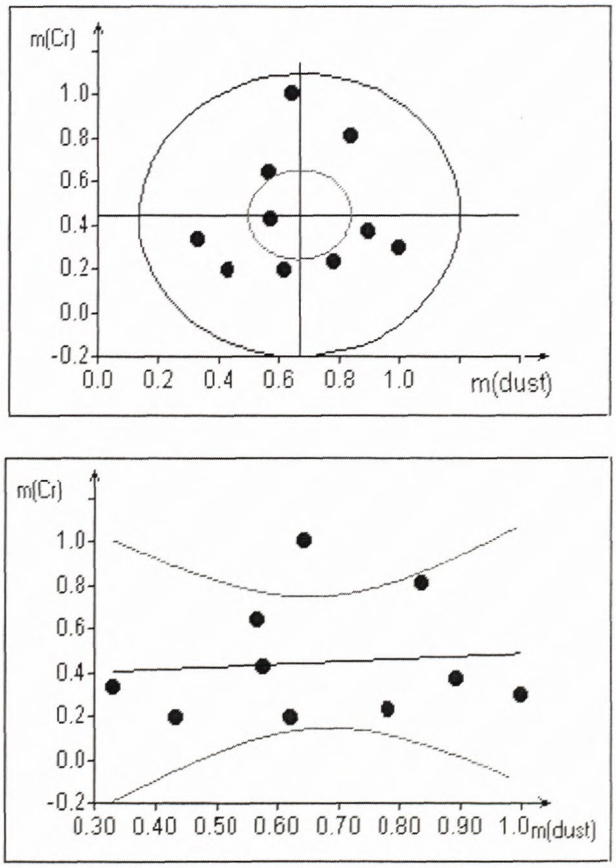


Fig. 12. The scatter diagram and the regression straight line for the Cr / dust amount ratio

this element and the all member of this group of elements not correlated with the amount of the dust. That means that this group is formed only the element background of the atmospherically dustiness, and is present by not typical pollutants. Lastly it is necessary to discuss the behavior of Pb. This element presents in the residential agglomeration a specific problem. The amount of this element (Fig. 13) shows extremely low correlation and zero regression. This phenomenon is caused by the fact that its genesis is footed not in the general dustiness but primarily in the amount of Pb containing additives in the exhaust of motor engines.

Conclusion

The validation of the dust fluctuation not only the total dust amount but also it is necessary take into accounts the predominant meteorological situations and the geographical abilities in the residential agglomerations and the given regions.

The N and S winds alternate in the funnel shaped region of the city Košice. The amount of W and E winds is irrelevant. These phenomena create two typical dustiness situations. The first case is characterized by prevailing N winds and is distinguished by the minimum of dustiness.

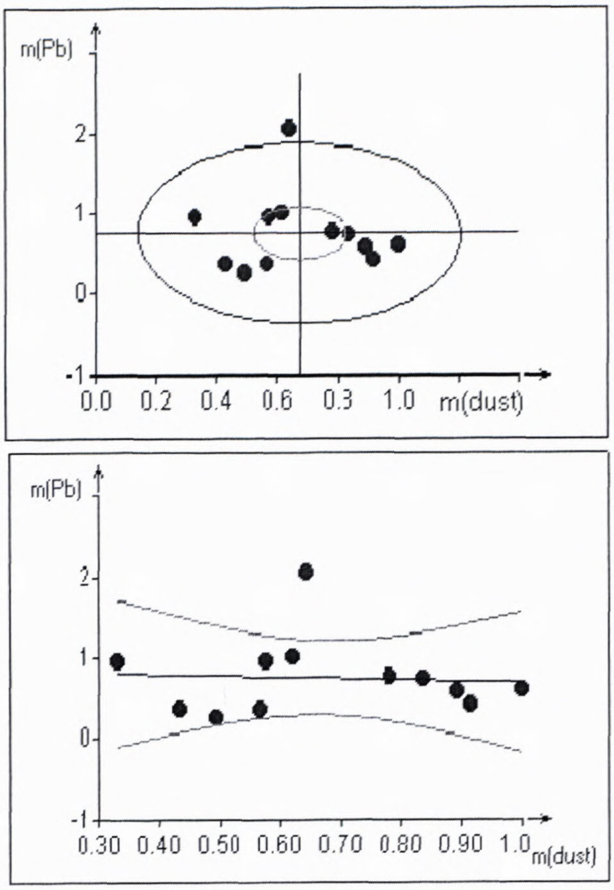


Fig. 13. The scatter diagram and the regression straight line for the Pb / dust amount ratio

The second case with balanced N and S winds is characterized by the maximum of dustiness. These phenomena is caused by the enhancing of the atmospherically dustiness with surface elements from the soil erosion in the southern part of the city Košice.

The amount of the components, mainly oxides and sulphates of metallic elements, is in the dust very variable. The subsidiary elements Fe, Mn, and Ti come mainly from the geological substratum and present the constant highest concentrations of dustiness. This well correlated with the total dustiness amount. The occurrence of the Cu and Zn come from the exhaust of pyrometallurgical factories in the valley of the river Hornad north-westly from Košice. These factories have campaign production character and therefore the amount of dust is very variable and its correlation with the total dust is also low. The amount of Cr and the other trace elements is maximal about one order lower as the amount of subsidiary elements. This element and the other trace elements created not typical and inconstant trace element background. The positions of the Pb in the dust are in the residential agglomerations very specific. The amount of this element shows low correlation and zero regression. This phenomenon is caused by the fact that its genesis is footed not in the general dustiness but primarily in the amount of Pb containing additives in the exhaust of motor engines.

Reference

Einax J., Danzer K. & Matherny M., 1991: Umweltanalytische und chemometrische Untersuchungen am Staubniederschlagen. Intern. J. Environ. Anal. Chem. 44, 185-196.

Flórián K.,& Pliešovská N., 1980: Multielement Spectrochemical Method for Pollution Control. Acta Chim. Hung. 103, 301-304.

Junge Ch. E., 1962: Air Chemistry and Radioactivity. Academis Press, New York

Kupka J., 2002: QC-Expert 2.5 Statistical Software. TrzloBzte, Ltd., Pardubice.

Malisa H., & Robinson J. W., 1979: Analysis of Airborne Particles by Physical Methods. CRC, Palm Beach.

VDI / DIN Handbuch: Reinhaltung der Luft, 1996: Determination of Dust Precipitation with Collecting Pots Made of Glass (Bergerhoff Method), Part 2, Beuth Verlag, Berlin.

Ure A. M., & Davidson C. M., 1985: Chemical speciation in the Environment. Blackie, London.

Slovak Geol. Mag., 9, 2 – 3(2003), 189 – 192

Monitoring of selected Elements in Wine and geochemical Characterization of Soil from Vineyards Regions in Slovakia

MILAN SUHAJ – MÁRIA KOREŇOVSKÁ – ĽUBOMÍR DAŠKO

Food Research Institute, Priemyselná 4, 824 75 Bratislava

Abstract. The results of monitoring of selected elements As, Cd, Cr, Hg, Ni and Pb in soils from 6 basic vineyards in Slovakia were compared to the data of selected monitored elements in Slovak wines with the aim of wines geographical authentication. Correlation analysis proofed that relation between contents of selected elements in wine is closely related with their content in soils almost all regions. The highest correlation level between composition of soil and wine exceeding 90 % were in Low Carpathians and Tokaj vineyard region. From the point of view of applicability of selected group of elements for vineyard regions and wine authenticity determination Principal Components Analysis as a statistical tool was used. Based on PCA method very high level of differentiation was achieved in the case of vineyards soils. Applying PCA method to distinguish geographic origin of wine from different vineyards regions the level of geographic authenticity was not so good. Proper selection of specific elements which could be useful for wine geographical traceability will be used in the next research of wine geographical authentication.

Key words: wine, soil, vineyards, authentication, elements

1. Introduction

There is evident increasing interest in food authenticity in relations to growing requirements on quality, food origin recognition, traceability and food safety. To meet all these requirements it is critical to improve knowledge of characteristic criteria of authenticity and specific quality markers. In accordance with these requirements EU adopted food legislation EC No. 178/2002, which defines duties to develop scientific methods relating to food risk assessment and food traceability procedures. There are many papers available related to wine origin traceability based on trace elements profile. Elements can be considered as good indicators of wine origin since they are not metabolized or modified during the vinification process (Arvanitozannis, 1999). Multi-element analysis using 35 elements determination by inductively coupled plasma mass spectrometry (ICP-MS) was used to classification of Spanish and English wines (Baxter, 1997). Eleven elements, K, Na, Ca, Mg, Fe, Cu, Zn, Mn, Li and Rb, were determined in dry and sweet wines bearing the denominations of origin of Canary Islands, Spain (Frías, 2002). Distribution of heavy metals (Pb, u, Zn and Cd) in the system soil – grapevine – grape was investigated by Angelova, 1999. The authenticity and geographical origin of wines produced in Slovenia were investigated by a combination of IRMS and SNIF-NMR methods and the stable isotope data were evaluated using principal component analysis (PCA) and linear discriminant analysis (LDA), (Ogrinc 2001). The usefulness of lanthanides or rare earth elements has also been clearly demonstrated since La, Ce, Pr, Nd, Eu, Gd, Tb, Ho, Er, Tm, Yb, Lu are some of the lanthanides successfully employed for distinction between regions (McCurdy, 1992).

There is food basket monitoring (FBM) in Slovakia since 1993 dedicated to monitor selected food additives and contaminants in the foodstuff with the aim to assess human loading with selected substances. In the monitoring database which is in the Food Research Institute (FRI) there are concentrations levels data of selected trace elements in Slovak wines from six vineyards (Low Carpathian, Nitra, South Slovakia, Central Slovakia, East Slovakia and Tokaj) which are defined by Decree of Ministry of Agriculture No. 153/1998 C L. on vineyards and viticulture. Vineyards in Slovakia cover in total 20 000 ha. Almost 80 % of vineyards are in the region of western Slovakia, 13 % in the central Slovakia and almost 7 % in eastern Slovakia. The soils in Low Carpathian region are skeletal, light, only slightly trapping water and well adsorbing energy from the sun. From the geology point of view, there are deep magnetites pararuls, but also biotic granites and granodiorits. South Slovakian vineyard region has the highest temperature with dry climate and mild winters. The soils are mostly light sandy up to middle hard unskeletal with deeper profile. Nitra vineyard region is heterogeneous from the geographical point of view. North regions are mostly skeletal soils with profile based on limestone, dolomites, quartzite and sandstones of Mesozoic. South and west parts dominate neogenic sediments with origin from south region. Geological base of soils from central Slovakian region is composed of neogenic sediments, shale and sandstones without skeleton. There are highly nutritive middle hard and hard soils.

ISSN 1335-096X

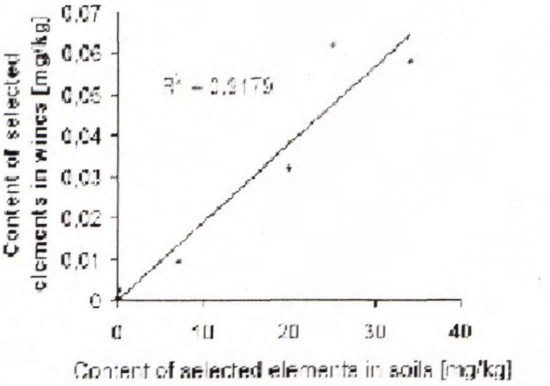


Fig. 1 Correlation of the content of selected elements in wines and soils from Low Carpathian Region

East Slovakian vineyard region is heterogeneous from the geological point of view. Under Vihorlat dominate hard, clay – mudstone soils, created on neogenic alluvial – pyroxenes and andesine. Vineyards located in limestone and caves region have rendezite skeletal soils with ripple slope relief. In Streda nad Bodrogom there are light sandy soils. The smallest region from the area point of view Tokaj has rocky, gravel, sandy-clay soils with higher content of skeleton. They were created on alluvial base from younger Paleozoic, on rezolits, andesine and their tuffites. Typical is higher acidity and high content of minerals (Hronský, 2001).

In this paper are evaluated analytical results of selected elements in wine from the monitoring databank. They are compared with geochemical characteristics of soils from vineyards regions. The aim is to find correlation with geographical origin of wine.

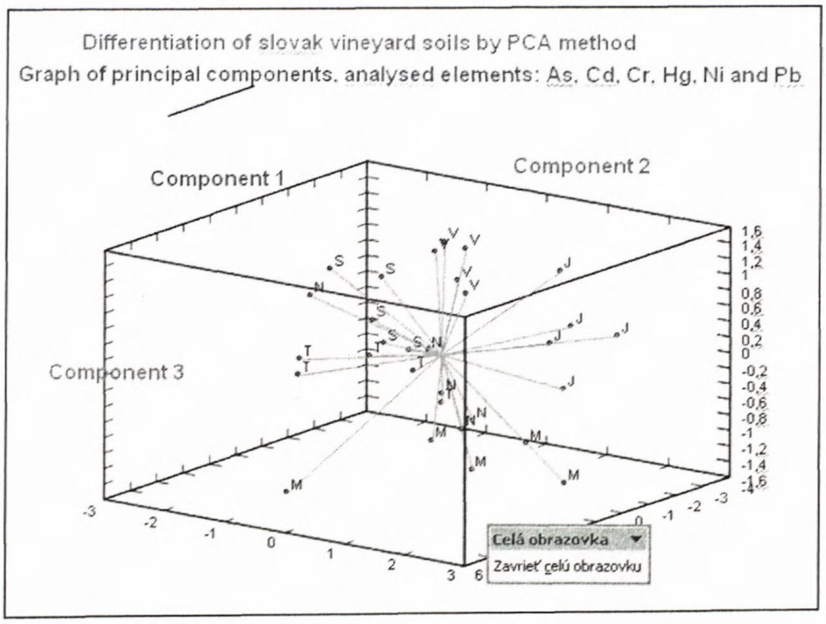


Fig. 2 Differentiation of Slovak vineyard soils by PCA methods

2. Materials and methods

The attempt to trace wine origin based on trace elements profile applying statistical identification of different vineyards regions of Slovakia is related to the results of food basket monitoring. We applied the data for wine and soil from vineyards regions from the Center for evaluation of presence of food additives and contaminants in Food Research Institute Bratislava and data on geochemical composition of soils from vineyards regions of Slovakia (Čurlík, 1999). We have taken into account only the wine regional origin no year of production, sort or other wine evaluation criteria. Statistical comparison and differentiation of 6 vineyards of Slovakia was based on results of content of selected elements As, Cr, Cd, Ni, Pb and Hg. I was studied correlation between content of trace elements in wine with relations to their content in soils from vineyards regions in Slovakia. We applied for basic statistical evaluation software Microsoft Excel 2002 and Unistat 4.53 for multivariate analysis (PCA). By PCA parallel projection of components by angles $\alpha = 126°$ and $\beta = 24°$ was applied.

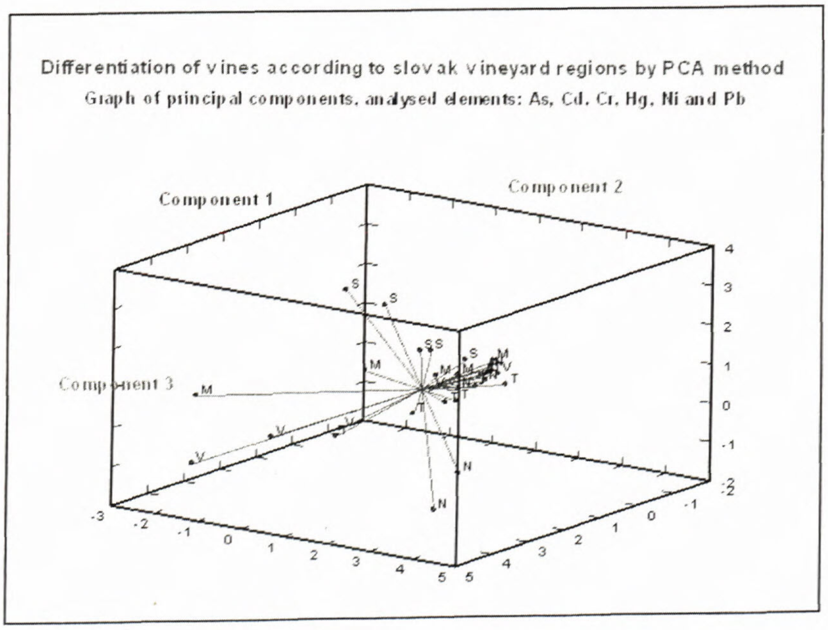


Fig. 3 Differentiation of some slovak vines by PCA method.

3. Results and discussions

The results of monitoring of selected elements in soils from 6 basic vineyards in Slovakia are in the Tables 1 and 2. Comparing the data of selected monitored elements in soil and wine remarkable correlation is evident. Correlation analysis proofed that relation between contents of

Table 1 Distribution of selected elements in soils from wine yards (WY) regions in Slovakia

Element	Elements distribution [mg/kg] in soils[1] in WY[2] Slovakia					
	J	M	N	S	V	T
Pb	3 – 13	20 – 69	13 – 30	16 – 30	13 – 20	16 – 30
As	4 – 7.2	7.2 – 16.2	7.2 – 9.9	5.3 – 7.2	3.3 – 5.3	5.3 – 9.9
Hg	0.02 – 0.05	0.05 – 0.14	0.03 – 0.08	0.05 – 0.14	0.03 – 0.08	0.05 – 0.14
Cr	46 – 85	34 – 101	67 – 125	85 – 101	85 – 101	67 – 101
Ni	25 – 44	25 – 44	16 – 33	16 – 33	25 – 33	16 – 25
Cd	0.1 – 0.4	0.3 – 0.4	0 – 0.2	0 – 0.2	0 – 0.3	0 – 0.2

[1] Čurlík, J. – Šefčík, P. (1999): Geochemical atlas of Slovakia. Part V: Soils. MŽP SR, VÚPaOP, Bratislava, 1999, 99 s.

[2] WY: Wine yards regions in Slovakia: J – South Slovakia, M – Low Carpathian, N – Nitra, S – Central Slovakia, V – East Slovakia, T – Tokaj

Table 2 Distribution of selected elements in wines from wine yards regions of Slovakia.

Element	Elements distribution [mg/kg] in wines from WY[1] regions in Slovakia Xmin – Xmax/Xaverage[2]					
	J	M	N	S	V	T
Pb	0.02–0.05 0.0386	0.002–0.08 0.0321	0.001–0.06 0.0261	0.09–0.2 0.1613	0.01–0.3 0.05	0.003–0.259 0.05
As	0.001–0.007 0.005	0.005–0.045 0.0095	0.002–0.026 0.0083	0.007–0.067 0.0025	0.002–0.01 0.005	0.001–0.005 0.003
Hg	ND	ND – 0,004 0.0007	ND – 0.002 0.0005	ND – 0.002 0.0003	ND – 0.003 0.0006	ND – 0.001 0.0004
Cr	ND	0.002–0.29 0.0584	0.002–0.18 0.065	ND – 0.06 0.0324	0.041–0.07 0.055	0.09
Ni	ND	0.03–0.14 0.0620	0.002–0.564 0.0961	ND–0.127 0.18	0.028–0.1 0.064	0.05
Cd	0.001–0.005 0.0023	0.001–0.025 0.0066	0.001–0.008 0.0023	0.001	0.001–1.642 0.0391	0.001–0.02 0.0084

[1] as in Table 1

[2] amount of samples n = 1 up to 100

Table 3 Correlation of content of As, Cd, Cr, Hg, Ni a Pb in wines and soils of vineyards regions of Slovakia

Wine yard region, correlation coefficient					
South Slovakia	Low Carpathian	Nitra	Central Slovakia	East Slovakia	Tokaj
0.8585	0.9581	0.7348	0.0801	0.8413	0.9122

selected elements in wine is closely related with their content in almost all regions. An example of this correlation is on the Figure No. 1 for Low Carpathian region, the survey of defined correlation coefficients is in the Table No. 3. The highest correlation level between composition of soil and wine exceeding 90 % were in Low Carpathians region and Tokaj region. Central Slovakian region was the region with very low level of correlation less than 8 %. It could be consequence of relatively small amount of results from this region available for vineyards and wines.

From the point of view of applicability of selected group of elements for determination of authenticity of vineyard regions and wine interesting tool is statistical evaluation. The aim of statistical evaluation applying the method of principal components (Principal Components Analysis – PCA) was the proper differentiation of vineyards and wines based on the regions. Based on PCA method very high level of differentiation was achieved in the case of vineyards soils, Figure 2. Its evident that based on statistical evaluation selected elements provide suitable data sours for reliable distinguish of vineyards except of Nitra region. When such reliable level of discrimination was achieved in soil data analysis, for wine data deducing from correlation patterns the results should by similar. But it is not the case. Applying PCA method to distinguish geographic origin of wine from different vineyards regions the level of geographic authenticity was not so good Figure 3. It is interesting, that most efficient segregation was achieved for wine from central Slovakia region which as only one was separated but in correlation analysis for wine from this region there was found the lowest level of correlation with the region soil matrix. It is evident that for identification of wine from different regions selected contaminated elements were not suitable choice.

Conclusions

It is evident that selected elements from Monitoring of food additives and contaminants As, Cd, Cr, Hg, Ni and Pb in soils from wine yards regions are suitable tool for geographical authenticity, which is interesting for soils traceability but not interesting for requirements of wine geographical origin authenticity. We are now focused for proper selection of specific elements which could be useful for wine geographical traceability.

Literature

Angelova, V. R., Ivanov, A. S. & Brajkov, D. M. (1999): Heavy metals (Pb, Cu, Zn and Cd) in the system soil – grapevine – grape. Journal of the Science of Food and Agriculture, 79: pp. 713–721.

Arvanitoyannis, I. S., Katsota, M. N., Psarra, E. P., Soufleros, E. H. & Kallithraka, S. (1999): Application of quality control methods for assessing wine authenticity: Use of multivariate analysis (chemometrics). Trends in Food science & Technology, 10: pp. 321–336.

Baxter, M. J., Crews, M. H., Dennis, M. J., Goodall, I. & Anderson, D. (1997): The determination of the authenticity of wine from its trace element composition. Food Chemistry, 60: pp. 443–450.

Čurlík, J. & Šefčík, P. (1999): Geochemical atlas of SR. Part V: Soils. MŽP SR, VÚPaOP, Bratislava, 99 p.

Frías, S., Conde, J. E., Rodríguey, M. A., Dohnal, V. and Trujillo, J. P. P. (2002): Metallic content of wines from the Canary Islands (Spain). Application of artificial neural networks to the data analysis. Nahrung/Food, 46: pp. 370–375.

Hronský, V. (2001): Slovak wines, BELIMEX, Bratislava, 118 p.

McCurdy, E. , Potter, D. & Medina, M. (1992): Trace elements in wines. Laboratory News, No. 9, pp. 10–11.

Ogrinc, N., Košir, I. J., Kocjančič, M., & Kidrič, J. (2001): Determination of authenticity, regional origin, and vintage of Slovenian wines using a combination of IRMS and SNIF-NMR Analyses. J. Agric. Food Chem. 49: pp. 1432–1440.

Slovak Geol. Mag., 9, 2– 3(2003), 193 – 196

Use of Chemical Analysis of Descending Spring Waters for Permeability and Transmissivity of the Rock Environment

STANISLAV OLEKŠÁK

Geological Survey of Slovak Republic, Markušovská cesta 1, Spišská Nová Ves

Abstract. Using of indirect method for evaluation of permeability and transmissivity on neovolcanic rocks of the Vihorlatské vrchy Mts., Slanské vrchy Mts. is presented in the paper. For evaluation was used hydrochemical method based on chemical analyses of descending spring waters and geomorphometric characteristics of territory. Achieved results of used method appear satisfactory.

Key words: descending spring water, neovolcanic rocks, indirect methods of evaluation hydraulic parameters of rocks, coefficient of hydraulic conductivity, coefficient of transmissivity

Introduction

Paper deals with possibility of use the chemical analyses of descending spring waters for regional assesment hydraulic parameters of neovolcanic rocks Vihorlatské vrchy Mts. and Slanské vrchy Mts. This method belongs to the group of indirect methods (Jetel, 1989, 1997a, 2002; Jetel & Kullman, 1987) for regional assesment hydraulic parameters of rocks. Indirect methods for estimation hydraulic parameters don´t use data from hydrodynamic tests, but different type data (baseflow, geomorphometric characteristics of territory, chemical composition descending spring water). When data are properly interpreted, they provide indirect informations about hydraulic parameters of rock enviroment.

Use of indirect methods is necessary for regional assesment hydraulic parameters of rocks when application of direct methods is not possible (borehole exploration of region is low, results of hydrodynamic tests were wrong interpreted).

Paper compares differences between estimates of direct and indirect hydrochemical method and evaluates application of hydrochemical method.

Permeability and transmissivity of neovolcanic rocksaccording the direct methods and systematic assumptions of hydrochemical method application

Permeability and transmissivity of Vihorlatské vrchy Mts. neovolcanic rocks elaborated Jetel (1997b) by direct methods. Permeability and transmissivity of Slanské vrchy Mts. neovolcanic rocks published Olekšák (2002) using borehole database from southern part of the territory (Jetel, 1993). Data are presented in tables 1 and 2.

Schematization of the formation of descending spring water chemical composition may be described as follows (Jetel, 1989, 2002)

Tab. 1 Distribution characteristics of coefficient of hydraulic conductivity k in the Vihorlatské vrchy Mts. (Jetel, 1997b) and the Slanské vrchy Mts. (Olekšák, 2002)

	n	R(k) m.s^{-1}	Md(k) m.s^{-1}	G(k) m.s^{-1}	G1 - G2 m.s^{-1}	E(k) m.s^{-1}
Vihorlatské vrchy Mts.	84			$1.4.10^{-5}$	$1.1.10^{-5}$ - $1.9.10^{-5}$	$3.5.10^{-5}$
Slanské vrchy Mts.	69	$1.6.10^{-7}$ - $1.1.10^{-3}$	$1.3.10^{-5}$	$1.1.10^{-5}$	$7.4.10^{-6}$ - $1.5.10^{-5}$	$3.7.10^{-5}$

Explanation: n=number of data; R(k)=range of k values; Md(k)=median of k; G(k)=geometric mean of k; G1, G2=lower and upper limit of 90 % confidence interval for the estimate of the geometric mean of the hydraulic conductivity k; E(k)=mathematical expectance of hydraulic conductivity k derived by Aitchison and Brown function

Tab. 2 Distribution characteristics of coefficient transmissivity T in the Vihorlatské vrchy Mts. (Jetel, 1997b) and the Slanské vrchy Mts. (Olekšák, 2002)

	n	R(T) m^2.s^{-1}	Md(T) m^2.s^{-1}	G(T) m^2.s^{-1}	G1 - G2 m^2.s^{-1}	E(T) m^2.s^{-1}
Vihorlatské vrchy Mts.	84	$2.6.10^{-5}$ - $3.5.10^{-2}$	$6.5.10^{-4}$	$6.7.10^{-4}$	$5.0.10^{-4}$ - $9.1.10^{-4}$	$1.9.10^{-3}$
Slanské vrchy Mts.	69	$5.7.10^{-6}$ - $2.3.10^{-2}$	$9.7.10^{-4}$	$7.1.10^{-4}$	$5.0.10^{-4}$ - $9.9.10^{-4}$	$2.3.10^{-3}$

Explanation: R(T) = range of T values; Md(T) = median of T; G(T) = geometric mean of T; G1, G2 = lower and upper limit of 90 % confidence interval for the estimate of the geometric mean of the transmissivity T; E(T) = mathematical expectance of transmissivity T derived by Aitchison and Brown function

Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava 2003 ISSN 1335-096X

- a relatively short vertical descent of infiltrated water through soil and unsaturated zone to the first groundwater body (saturated part of near-surface zone),
- a descending-lateral groundwater movement in the saturated part of the near-surface zone over the slope from infiltration to the spring,
- an approximate accordance between the average dip of the first groundwater body level during the descending-lateral movement with the average dip of ground surface (slope),
- a quasi-linear growth of M_i concentration of the considered i component with the lateral filtration length L.

The resulting concentration M_i of the i component is determined by the relation

$$M_i = M_{i0} + \Delta M_i \qquad (1)$$

where M_{i0} = initial concentration entering the process of the quasi-linear growth – i. e. concentration in water after the vertical descent through the soil and unsaturated zone to the lateral flow, ΔM_i = increase in concentration during lateral flow from infiltration to the spring.

Increase in concentration ΔM_i can be expressed (Jetel, 1989)

$$\Delta M_i = (W_i/k) \cdot (m_A/m_e) \cdot (L/J) \qquad (2)$$

where w_i = i-component transition rate to solution from rock volume unit (interaction rate) ($g.m^{-3}.s^{-1}$), k = average effective value of ceofficient of hydraulic conductivity of near-surface zone ($m.s^{-1}$), m_A = filtration cross-section effectiveness („effective areal porosity") (-), m_e = chemically effective porosity (-), L = average length of lateral filtration path of near-surface zone (m), J = piezometric gradient, average dip of the first groundwater body approximated by average dip of terrain surface (slope) between the start of infiltration and outflow.

For each other studied component i we will gather linear regressing equation of the type

$$M_i = a_i + b_i \cdot (L/J) \qquad (3)$$

M_i values we will gain from chemical analyses of spring waters, the geomorphometric characteristics L a J may be read from a level line map. For L value is usuallly used a half-distance from the spring to the infiltration (Jetel, 1989).

The next, relationship between M_i and L/J are studied for M_i = T. D. S., Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, $SO4^{2-}$, Cl^-.

Average hydraulic conductivity k_{ch} of the near-surface zone in the feeding area of descending springs according to the value of the regression coefficient b_i of the equation of (3) is determined by the equation

$$k_{ch}=(1/b_i).w_i.m_A/m_e \qquad (4)$$

Practical application of the method is only possible at knowledge or reliable estimation of the values of interaction rates w_i and m_A/m_e. For the sake of comparability of single regions, constant value $m_A/m_e = 0{,}4$ (Jetel et al., 1993) was accepted. Probable range and medians of w_i are in table 3.

From the k_{ch} estimates we will derive estimate of the near-surface zone transmissivity:

$$T_{ch} = k_{ch} \cdot H \qquad (5)$$

where H = accepted effective thickness of water-saturated part of near-surface zone (m).

Tab. 3: Probable range and medians of interaction rates w_i ($g.m^3.s^{-1}$) according to present-day knowledge (Jetel et al., 1993)

w_i	w(min)	w(max)	Md(w)
w(CM)	$5.8.10^{-8}$	$7.1.10^{-7}$	$2.0.10^{-7}$
w(Ca)	$8.4.10^{-9}$	$1.2.10^{-7}$	$2.0.10^{-8}$
w(Mg)	$2.2.10^{-9}$	$1.4.10^{-8}$	$1.1.10^{-8}$
w(Na)	$5.8.10^{-9}$	$6.2.10^{-9}$	$6.0.10^{-9}$
w(HCO_3)	$4.5.10^{-8}$	$5.9.10^{-7}$	$1.0.10^{-7}$
w(SO_4)	$3.6.10^{-8}$	$5.9.10^{-8}$	$5.1.10^{-8}$
w(Cl)	$3.4.10^{-8}$	$4.8.10^{-8}$	$4.1.10^{-8}$

Explanation: w(min), w(max), Md(w)=probable minimum, maximum and median iterraction rate wi; CM=total dissolved solid T.D.S.

First experiences with practical application of presented method in Vihorlatské vrchy Mts. neovolcanic rocks (table 4) were published by Jetel (1989).

Tab. 4 Relation of T. D. S. ($mg.l^{-1}$), concentration HCO_3^- ($mg.l^{-1}$), Ca^{2+} ($mg.l^{-1}$) to parameter L/J in Vihorlatské vrchy Mts. (Jetel, 1989)

i	n	r^2	a_i ($g.m^{-3}$)	b_i ($g.m^{-4}$)
CM	22	0.826	70.9	0.0182
$HCO3^-$	22	0.859	7.4	0.0122
Ca^{2+}	22	0.820	6.5	0.00182

Explanation: r^2 = determination coefficient; a_i = locating regression constant; b_i = regression coefficient

Practical application of average permeability and transmisivity estimate method from hydrochemical and geomorphometric characteristics of descending springs

Basic data derived from application of hydrochemical method in neovolcanic rocks are in table 5.

Basic statistical processing of data from the table 5 is in the table 6 (only data of higher r^2 values were elaborated).

From the table 6 results, that in Vihorlatské vrchy Mts. differences of estimates of mean values between k_{ch} (from hydrochemical method) and G(k) (from direct method) were lowest for mean values (geometric mean, arithmetic mean and median) of MA(k_{ch}). These mean values occur within the G1-G2 interval (table 1). Estimates of mean values k_{ch} from Max(k_{ch}) values are slightly overestimated in compare with values of G1-G2 interval. Estimates of mean values k_{ch} from Md(k_{ch}) values are more underestimated in compare with values of G1-G2 interval.

In Slanské vrchy Mts., differences of estimates of mean values between k_{ch} and G(k) were least for arithmetic mean and median of Md(k_{ch}) values. These mean values occur within the G1-G2 interval (table 1). Estimates of mean values k_{ch} from Max(k_{ch}) values are overestimated in compare with values of G1-G2 interval. Estimates of mean values k_{ch} from MA(k_{ch}) values are

Tab. 5 Relation of T.D.S. ($mg.l^{-1}$) and concentrations of selected ions ($mg.l^{-1}$) to parameter L/J in Vihorlatské vrchy Mts, Slanské vrchy Mts. and estimates of coefficient of hydraulic conductivity k_{ch} according the type of interaction rates

<table>
<tr><td colspan="9">VIHORLATSKÉ VRCHY Mts. (JETEL, 1989)</td></tr>
<tr><td>i</td><td>n</td><td>r^2</td><td>a_i ($g.m^{-3}$)</td><td>b_i ($g.m^{-4}$)</td><td>Min(k_{ch}) ($m.s^{-1}$)</td><td>Max(k_{ch}) ($m.s^{-1}$)</td><td>Md(k_{ch}) ($m.s^{-1}$)</td><td>MA(k_{ch}) ($m.s^{-1}$)</td></tr>
<tr><td>CM</td><td>22</td><td>0.826</td><td>70.9</td><td>0.0182</td><td>$1.27.10^{-6}$</td><td>$1.56.10^{-5}$</td><td>$4.40.10^{-6}$</td><td>$1.00.10^{-5}$</td></tr>
<tr><td>HCO_3</td><td>22</td><td>0.859</td><td>7.4</td><td>0.0122</td><td>$1.48.10^{-6}$</td><td>$1.93.10^{-5}$</td><td>$3.28.10^{-6}$</td><td>$1.13.10^{-5}$</td></tr>
<tr><td>Ca</td><td>22</td><td>0.820</td><td>6.5</td><td>0.0018</td><td>$1.85.10^{-6}$</td><td>$2.64.10^{-5}$</td><td>$4.40.10^{-6}$</td><td>$1.54.10^{-5}$</td></tr>
<tr><td colspan="9">VIHORLATSKÉ VRCHY Mts.</td></tr>
<tr><td>i</td><td>n</td><td>r^2</td><td>a_i ($g.m^{-3}$)</td><td>b_i ($g.m^{-4}$)</td><td>Min(k_{ch}) ($m.s^{-1}$)</td><td>Max(k_{ch}) ($m.s^{-1}$)</td><td>Md(k_{ch}) ($m.s^{-1}$)</td><td>MA(k_{ch}) ($m.s^{-1}$)</td></tr>
<tr><td>CM</td><td>16</td><td>0.656</td><td>78.444</td><td>0.0145</td><td>$1.60.10^{-6}$</td><td>$1.96.10^{-5}$</td><td>$5.52.10^{-6}$</td><td>$1.26.10^{-5}$</td></tr>
<tr><td>HCO_3</td><td>16</td><td>0.720</td><td>12.659</td><td>0.0088</td><td>$2.05.10^{-6}$</td><td>$2.68.10^{-5}$</td><td>$4.55.10^{-6}$</td><td>$1.57.10^{-5}$</td></tr>
<tr><td>SO_4</td><td>16</td><td>0.115</td><td>11.231</td><td>-0.0007</td><td>-2.06E-05</td><td>-3.37E-05</td><td>-2.9E-05</td><td></td></tr>
<tr><td>Cl</td><td>16</td><td>0.127</td><td>1.856</td><td>-0.00008</td><td>-1.70E-04</td><td>-2.40E-04</td><td>-2.1E-04</td><td></td></tr>
<tr><td>Ca</td><td>14</td><td>0.631</td><td>7.507</td><td>0.0015</td><td>$2.24.10^{-6}$</td><td>$3.20.10^{-5}$</td><td>$5.33.10^{-6}$</td><td>$1.87.10^{-5}$</td></tr>
<tr><td>Na</td><td>16</td><td>0.374</td><td>2.808</td><td>0.0003</td><td>$7.73.10^{-6}$</td><td>$8.27.10^{-6}$</td><td>$8.00.10^{-6}$</td><td></td></tr>
<tr><td>Mg</td><td>15</td><td>0.696</td><td>1.408</td><td>0.0004</td><td>$2.20.10^{-6}$</td><td>$1.40.10^{-5}$</td><td>$1.10.10^{-5}$</td><td>$1.25.10^{-5}$</td></tr>
<tr><td colspan="9">SLANSKÉ VRCHY Mts.</td></tr>
<tr><td>i</td><td>n</td><td>r^2</td><td>a_i ($g.m^{-3}$)</td><td>b_i ($g.m^{-4}$)</td><td>Min(k_{ch}) ($m.s^{-1}$)</td><td>Max(k_{ch}) ($m.s^{-1}$)</td><td>Md(k_{ch}) ($m.s^{-1}$)</td><td>MA(k_{ch}) ($m.s^{-1}$)</td></tr>
<tr><td>CM</td><td>35</td><td>0.636</td><td>126.430</td><td>0.0073</td><td>$3.18.10^{-6}$</td><td>$3.89.10^{-5}$</td><td>$1.10.10^{-5}$</td><td>$2.48.10^{-5}$</td></tr>
<tr><td>HCO3</td><td>31</td><td>0.707</td><td>27.908</td><td>0.0066</td><td>$2.73.10^{-6}$</td><td>$3.58.10^{-5}$</td><td>$6.06.10^{-6}$</td><td>$2.09.10^{-5}$</td></tr>
<tr><td>SO4</td><td>35</td><td>0.028</td><td>25.533</td><td>0.0008</td><td>$1.80.10^{-5}$</td><td>$2.95.10^{-5}$</td><td>$2.55.10^{-5}$</td><td></td></tr>
<tr><td>Cl</td><td>35</td><td>0.091</td><td>2.433</td><td>0.0001</td><td>$1.36.10^{-4}$</td><td>$1.92.10^{-4}$</td><td>$1.64.10^{-4}$</td><td></td></tr>
<tr><td>Ca</td><td>32</td><td>0.687</td><td>13.644</td><td>0.0009</td><td>$3.73.10^{-6}$</td><td>$5.33.10^{-5}$</td><td>$8.89.10^{-6}$</td><td>$3.11.10^{-5}$</td></tr>
<tr><td>Na</td><td>35</td><td>0.047</td><td>4.753</td><td>0.0001</td><td>$2.32.10^{-5}$</td><td>$2.48.10^{-5}$</td><td>$2.40.10^{-5}$</td><td></td></tr>
<tr><td>Mg</td><td>31</td><td>0.610</td><td>3.320</td><td>0.0003</td><td>$2.93.10^{-6}$</td><td>$1.87.10^{-5}$</td><td>$1.47.10^{-5}$</td><td>$1.67.10^{-5}$</td></tr>
</table>

Explanation: Min(k_{ch}) = coefficient of hydraulic conductivity derived from w(min); Max(k_{ch}) = coefficient of hydraulic conductivity derived from w(max); Md(k_{ch}) = coefficient of hydraulic conductivity derived from Md(w); MA(k_{ch}) = arithmetic mean of Max(k_{ch}) and Md(k_{ch}) – i. e. MA(k_{ch}) = (Max(k_{ch})+Md(k_{ch}))/2

Tab. 6 Statistical analyse of neovolcanic rocks permeability from the hydrochemical method data

<table>
<tr><td colspan="11">Vihorlatské vrchy Mts. (Jetel, 1989)</td></tr>
<tr><td></td><td>G</td><td>G/G(k)</td><td>Md</td><td>Md/G(k)</td><td>M</td><td>M/G(k)</td><td>Vr^2</td><td>Vr^2/G(k)</td><td>Vnr^2</td><td>Vnr^2/G(k)</td></tr>
<tr><td>Max(k_{ch}) ($m.s^{-1}$)</td><td>$2.00.10^{-5}$</td><td>1.43</td><td>$1.93.10^{-5}$</td><td>1.38</td><td>$2.04.10^{-5}$</td><td>1.46</td><td>$2.04.10^{-5}$</td><td>1.46</td><td></td><td></td></tr>
<tr><td>Md(k_{ch}) ($m.s^{-1}$)</td><td>$3.99.10^{-6}$</td><td>0.28</td><td>$4.40.10^{-6}$</td><td>0.31</td><td>$4.02.10^{-6}$</td><td>0.29</td><td>$4.01.10^{-6}$</td><td>0.29</td><td></td><td></td></tr>
<tr><td>MA(k_{ch}) ($m.s^{-1}$)</td><td>$1.20.10^{-5}$</td><td>0.86</td><td>$1.13.10^{-5}$</td><td>0.81</td><td>$1.22.10^{-5}$</td><td>0.87</td><td>$1.22.10^{-5}$</td><td>0.87</td><td></td><td></td></tr>
<tr><td colspan="11">Vihorlatské vrchy Mts.</td></tr>
<tr><td></td><td>G</td><td>G/G(k)</td><td>Md</td><td>Md/G(k)</td><td>M</td><td>M/G(k)</td><td>Vr^2</td><td>Vr^2/G(k)</td><td>Vnr^2</td><td>Vnr^2/G(k)</td></tr>
<tr><td>Max(k_{ch}) ($m.s^{-1}$)</td><td>$2.20.10^{-5}$</td><td>1.57</td><td>$2.32.10^{-5}$</td><td>1.66</td><td>$2.31.10^{-5}$</td><td>1.65</td><td>$2.30.10^{-5}$</td><td>1.64</td><td>$2.28.10^{-5}$</td><td>1.63</td></tr>
<tr><td>Md(k_{ch}) ($m.s^{-1}$)</td><td>$6.19.10^{-6}$</td><td>0.44</td><td>$5.43.10^{-6}$</td><td>0.39</td><td>$6.60.10^{-6}$</td><td>0.47</td><td>$6.63.10^{-6}$</td><td>0.47</td><td>$6.59.10^{-6}$</td><td>0.47</td></tr>
<tr><td>MA(k_{ch}) ($m.s^{-1}$)</td><td>$1.46.10^{-5}$</td><td>1.05</td><td>$1.41.10^{-5}$</td><td>1.01</td><td>$1.49.10^{-5}$</td><td>1.06</td><td>$1.48.10^{-5}$</td><td>1.06</td><td>$1.47.10^{-5}$</td><td>1.05</td></tr>
<tr><td colspan="11">Slanské vrchy Mts.</td></tr>
<tr><td></td><td>G</td><td>G/G(k)</td><td>Md</td><td>Md/G(k)</td><td>M</td><td>M/G(k)</td><td>Vr^2</td><td>Vr^2/G(k)</td><td>Vnr^2</td><td>Vnr^2/G(k)</td></tr>
<tr><td>Max(k_{ch}) ($m.s^{-1}$)</td><td>$3.43.10^{-5}$</td><td>3.12</td><td>$3.73.10^{-5}$</td><td>3.39</td><td>$3.67.10^{-5}$</td><td>3.33</td><td>$3.71.10^{-5}$</td><td>3.38</td><td>$3.73.10^{-5}$</td><td>3.39</td></tr>
<tr><td>Md(k_{ch}) ($m.s^{-1}$)</td><td>$9.65.10^{-6}$</td><td>0.88</td><td>$9.92.10^{-6}$</td><td>0.90</td><td>$1.01.10^{-5}$</td><td>0.92</td><td>$9.97.10^{-6}$</td><td>0.91</td><td>$9.99.10^{-6}$</td><td>0.91</td></tr>
<tr><td>MA(k_{ch}) ($m.s^{-1}$)</td><td>$2.28.10^{-5}$</td><td>2.07</td><td>$2.29.10^{-5}$</td><td>2.08</td><td>$2.34.10^{-5}$</td><td>2.13</td><td>$2.36.10^{-5}$</td><td>2.14</td><td>$2.37.10^{-5}$</td><td>2.15</td></tr>
</table>

Explanation: G = geometric means; Md = medians; M = arithmetic means; Vr^2 = weighted arithmetic means after determination coefficient r^2; Vnr^2 = weighted arithmetic means after conjunctions of data number n and relevant determination coefficients r^2 - i.e. (n. r^2)

Tab. 7 Transmissivity neovolcanic rocks derived from hydrochemical method (H = 42 m)

	$T_{ch}(G_{MA})$	$T_{ch}(G_{MA})/G(T)$	$T_{ch}(Md_{MA})$	$T_{ch}(Md_{MA})/G(T)$	$T_{ch}(M_{MA})$	$T_{ch}(M_{MA})/G(T)$
Vihorlatské vrchy Mts. (from data of Jetel, 1989)	$5.04.10^{-4}$	0.75	$4.75.10^{-4}$	0.71	$5.12.10^{-4}$	0.76
Vihorlatské vrchy Mts.	$6.13.10^{-4}$	0.92	$5.92.10^{-4}$	0.88	$6.26.10^{-4}$	0.93
Slanské vrchy Mts.	$9.58.10^{-4}$	1.35	$9.62.10^{-4}$	1.35	$9.83.10^{-4}$	1.38

Explanation: Tch = koefficient of transmissivity derived from k_{ch}: G_{MA} = geometric mean of kch calculated from MA(k_{ch}); Md_{MA} = median of kch calculated from MA(k_{ch}); M_{MA} = arithmetic mean of kch calculated from MA(k_{ch})

also overestimated in compare with values of G1-G2 interval.

For calculation of k_{ch} in neovolcanic rocks is recommended to use choose some mean value (geometric mean, arithmetic mean, median) for MA(k_{ch}) values as a resultant mean value of coefficient of hydraulic conductivity, despite the fact that in Slanské vrchy Mts. the least difference is between G(k) and k_{ch} derived from mean values of Md(k_{ch}). In this case for calculation of transmissivity coefficient T_{ch} from hydrochemical method after formula (5), we recommend to use empirically determined value of H = 42 m (accepted effective thickness of water-saturated part of near-surface zone). Data are shown in table 7. By substituting value H=42 m it is secured, that almost all estimates of mean value T_{ch} are in G1-G2 interval for 90 % confidence of the estimate for geometric mean of transmissivity T (table 2).

Conclusion

Application hydrochemical method based on chemical composition descending spring water and geomorphometric characteristics for regional assessment of hydraulic parameters of neovolcanic rocks in Vihorlatské vrchy Mts. and Slanské vrchy Mts confirms, that method is usable in neovolcanic rock regions. Ions HCO_3^-, Ca^{2+}, Mg^{2+}, a CM are decisive for estimate of mean value k_{ch}. In Vihorlatské vrchy Mts., differences of estimates of mean values between k_{ch} and G(k) were lowest for geometric mean, arithmetic mean and median of MA(k_{ch}) values.

In Slanské vrchy Mts., differences of estimates of mean values between k_{ch} and G(k) were least for arithmetic mean and median of Md(k_{ch}) values.

For calculation of k_{ch} in neovolcanic rocks of Slovakia it is recommended to use above mentioned process and choose some mean value (geometric mean, arithmetic mean, median) for MA(k_{ch}) values as a resultant mean value of coefficient of hydraulic conductivity. Recommended value for H (accepted effective thickness of water-saturated part of near-surface zone) is 42 m.

For improvement of process of representative mean value selection (coefficient of hydraulic conductivity) from hydrochemical method in neovolcanic rock areas it will be necessary to apply presented method in other neovolcanic regions of Slovakia.

Literature

Jetel, J., 1989: Relationship between hydrogeochemical characteristics of near-surface zone of rock massif and hydrodynamic conditions. Západ. Karpaty, Sér. Hydrogeol. inž. Geol. 8. 67-104.

Jetel, J., 1993: Priepustnosť a prietočnosť neovulkanitov v južnej časti Slanských vrchov. Geol. Práce, Spr. (Bratislava), 98. 83-93.

Jetel, J., 1997a: Metodické postupy hodnotenia priemernej prietočnosti a priepustnosti v horských oblastiach nepriamymi metódami. Manuskript – archív ŠGÚDŠ, Bratislava. 85 s.

Jetel, J., 1997b: Hydrogeológia. In: Žec, B. (ed.), Vysvetlivky ku geologickej mape Vihorlatských a Humenských vrchov. Vydavateľstvo Dionýza Štúra, Bratislava. 178-193.

Jetel, J., 2002: Hodnotenie priemernej prietočnosti a priepustnosti v horských územiach nepriamymi metódami. Podzemná voda č. 2, ročník 7. 24-30.

Jetel, J. & Kullman, E., 1987: Nepriame stanovenie priemernej prietočnosti horninových telies pre zostavovanie hydrogeologických máp. Manuskript – archív ŠGÚDŠ, Bratislava. 83 s.

Jetel, J., Nemčok, J. & Tkáč, J., 1993: Hydrogeologický výskum Spišskej Magury – záverečná správa. Manuskript – archív ŠGÚDŠ, Bratislava. 222 s.

Olekšák, S., 2002: Priepustnosť a prietočnosť neovulkanitov vybraných území Slovenska. Podzemná voda č.1, ročník 8. 5-16.

Slovak Geol. Mag., 9, 2 – 3 (2003), 197 – 199

Old Metallurgical Slag near the abandoned Smolník Mine (Slovakia) and its Impact on the Environment

STANISLAV ŠOLTÉS, OTÍLIA LINTNEROVÁ and PETER ŠOTTNÍK

Dept. of Mineral Deposits, Comenius University, Faculty of Nat. Sci., Mlynská Dolina,
842 15 Bratislava, Slovak Republic, e-mail: soltes@fns.uniba.sk lintnerova@fns.uniba.sk sottnik@fns.uniba.sk

Abstract. The old metallurgical slag is northeast of the village Smolník by the stream Smolník. Composition of the slag was studied by optical microscopy, X-ray diffraction, chemical analyses and by electron microprobe analyser. Laboratory leaching experiments were done to find out behaviour of elements in the weatherig process. In the experiment there were leached fractions 0,8-4 mm in diameter in different solutions: distilled water, HNO_3 solution and citrate solution. The ratio solid/solution was 1/10 and the chemical analyses were performed in periods 1, 5, 10, 15, 20, 25 and 30 days. The slag is composed mainly from olivines and spinels. Citrate solution reached most metal contents leached from slag material. Water is able to leach only small concentrations of metals from slag. Generally Fe, Cu and Zn are most leachable in to the solution, Mn and Pb only slightly. Cu and As content in plants growing on the slag are exceeding the normal values in all analysed samples. Pb in all samples was below the normal concentration. Zn acceptable values were exceeded only in alder and grass.

Key words: slag, Smolník, leaching experiment, heavy metals

Introduction

Old mining town Smolník (eastern Slovakia) (Fig. 1) and surrounding countryside is well known with its mining wastes and acid water accident in 1994 (Jaško et al., 1996). Pyrite-chalcopyrite mines were mined for centuries till 1991. There is also an old metallurgical slag northeast of village Smolník. The slag come from old smelter in Smolnícka Huta village. This slag is next to the stream Smolník and it can have potentially harmful impact on the environment because this material contain high concentrations of heavy metals (Cu, Sn, Pb, Mn, Co, Zn, As). Metallurgical slag was often used for road constructions. It´s easy to find it in many road material in environ of Smolník and Smolnícka Huta villages. It´s important to determine the stability of heavy metals in slag material and possible release of contaminants in weathering conditions (Ettler et al.,1999, Ettler et al., 2001). Specific plants with adaptibility to heavy metals are growing on the slag and on the mine heaps also.

Methods

The mineralogical composition of slag was studied in thin and polished sections by transmitted and reflected light microscopy, X-ray diffraction (diffractometer Philips PW 1710), scanning electron microscopy, and by electron microprobe analyser (Cameca SX100).

By the leaching experiment were used 5g of sieved crushed slag material (grain size 0,8 – 4 mm) leached by different solutions for periods 1, 5, 10, 15, 20, 25 and 30 days. Used solutions were: distilled water (initial pH 5,8), HNO_3 solution (initial pH 1,6) was prepared from 1 ml of concentrated HNO_3 and 500 ml of distilled water, citrate solution was prepared from 46,5 ml of citrate acid (0,1 M) with 3,5 ml of citrate sodium (0,1 M) diluted with 100 ml of distilled water (initial pH 2,7). For each sample (5 g of slag) were added 50 ml of solution. The samples were shaken by table shaker, by ambient temperature, without acces of light. Measurements of conductivity, Eh and pH (in periods 1, 5, 10, 15, 20, 25 and 30 days) were performed with MC 126 conductivity meter Mettler Toledo, Redox potential and pH meter Mettler Toledo 1120. The glass electrode was calibrated at 25°C using Mettler-Toledo pH buffer solutions at pH of 4.01 and 7.00 and Mettler Toledo redox buffer solution. Leachates were filtered through 0,45 μm Millipore filter and stored in refrigerator until analyses. Leachate from each sample was analysed for Fe, Mn, Cu, Pb, Zn by atomic absorbtion spectrophotometry (AAS) and inductively coupled plasma atomic emission spectroscopy (AES-ICP). Consequential data were calculated to quantity of leached elements from 1 kg of slag material.

The slag material, ochres and soil from slag were digested with nitric acid at 95 şC for 2 h and Fe, Mn, Al, Cu, Pb, Zn, As, Co concentrations were analysed using ICP-AES.

The plants - spruce (needles), alder (leaves), grass (above-ground part), heather (above-ground part)) and moss (above-ground part) found on slag were dried and analysed by AAS.

Results

The main detected minerals in slag material are olivines and spinels (Fig. 2).

Leaching Experiment: H_2O (Fig. 3): The water leached most Cu, Fe and Zn. Volume of Cu and Zn in the water raised only slowly. Fe and Mn precipitated and dissolved again. Pb is not leached by the water.

Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava 2003 ISSN 1335-096X

Fig. 1 Localisation of Smolník village.

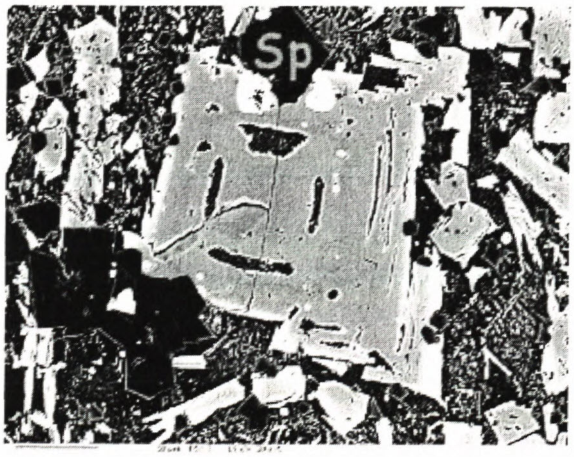


Fig. 2. Olivines (Ol) and Spinels (Sp) are the main minerals of slag.

HNO_3 (Fig. 4): The highest concentrations leached by HNO_3 solution has Fe. The diagram of Fe concentration copy essentially pH values (intense increase and afterwards slowly decrease). Cu achieve also high concentrations. The concentration of Cu raised with time and afterwards Cu partly precipitated. Zn as well but slower. Pb and Mn in HNO_3 solution have relatively low concentrations but stable.

Citrate solution (Fig. 5): Volume of leached Fe achieve very high concentrations with highest increase in first days of experiment, whatever this exactly matching the pH values. Cu is leached slowly in first days and after 10 days the concentration raised fast and after 25 days partly precipitated. Zn after fast release into the solution slowly precipitated. Pb and Mn after slowly increase of concentration were stable in solution.

Nitric acid digestion: In ochres on slag material are higher concentrations of Al, Cu, Mn, Co and As mobilised to the solution by nitric acid compared to slag material. It means that heavy metals are concentrated in ochres. In soil on slag are highly concentrated Pb and As (Fig. 6).

Plants: Cu and As content in plants growing on the slag are exceeding the normal values in all analysed samples. The moss have the most extreme As, Al and Fe contents. Zn is accumulating in leaves the most – alder exceeds the normal limit 15 times. Grass has extremely high content of Cu – the limit is 40 times exceeded. In generally the trees have lover content of metals together compared with moss, heather and grass (Fig. 7).

Discussion

The goal of this experiment was to simulate weathering process on slag and first to compare effect of different solutions on slag material. As we expected distilled water leached the lowest concentrations of metals from slag material and citrate solution which correspond to organic acids naturally present in the soil leached the highest concentrations of metals. This let us to say that high concentrations of metals released by acide solutions from slag aren´t from sulphates leachable by water. (Because the slag was before experiment washed by distilled water to focus only to pure slag material.)

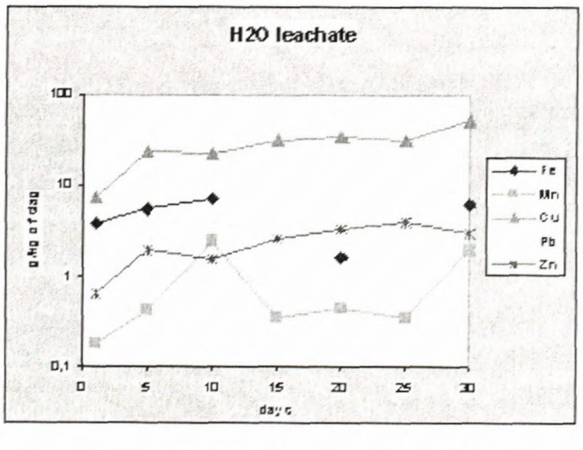


Fig. 3. Concentrations of metals leached by H_2O.

The concentrations of metals in leachate depends on stability fields of metals and the fall of Fe, Cu, Zn and Mn in the leachate is controlled by precipitation and absorption processes. The metals remain on filters if there were precipitated aggregates bigger than 0,45 µm.

The metals (mainly Fe, Cu and Zn) are leached from slag material in to the solution. Part of this solutions integrate with stream waters poluted with acid mine drainage (Šottník et al., 2002) and part of it concentrating in soil or ochres.

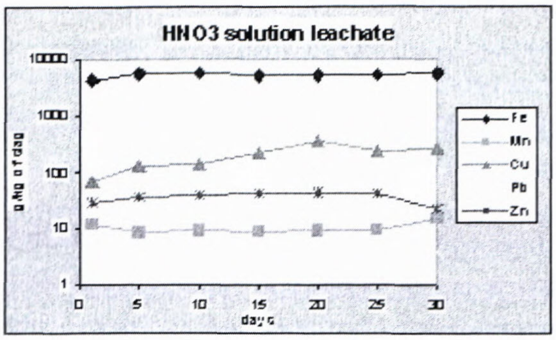


Fig. 4. Concentrations of metals leached by HNO_3 solution

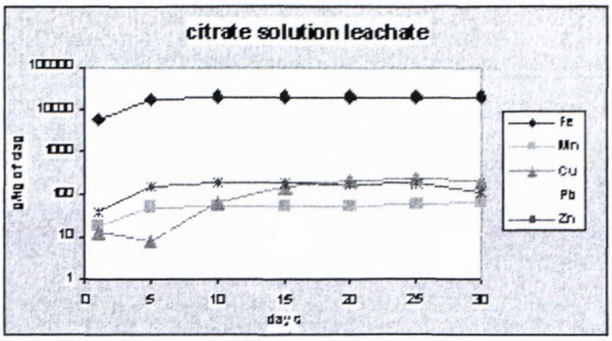


Fig. 5. Concentrations of metals leached by citrate solution

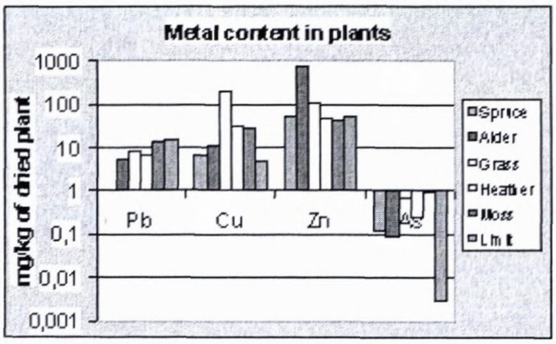


Fig. 6. Concentrations of metals in plants growing on slag compared with limit concentrations

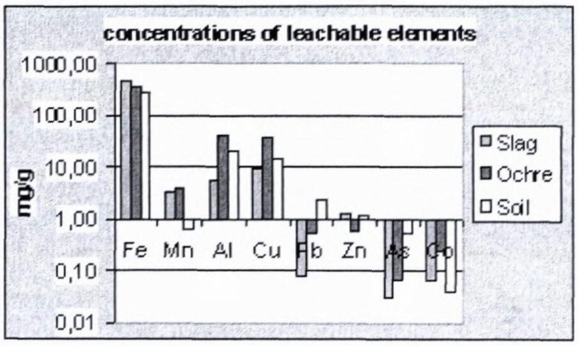


Fig. 7. Concentrations of metals released from slag, ochre and soil by nitric acid digestion

Conclusions

Citrate solution leached most metals from slag material. Water is able to leach only small concentrations of metals from slag. Generally Fe, Cu and Zn are most leachable in to the solution, Mn and Pb only slightly.

This results do not represent really natural processes because the experiment was done as "batch experiment" and the natural system is open.

Acknowledgments

This work was supported by Slovak Ministry of Education and Join Research Centre Institute for Environment Susstainability Ispra, Varese. Our project "Physico-Chemical properties and Environmental Impact of Mining Wastes in Slovakia" is one part of project "Environmental Impact of Toxic Mining Wastes in Pre-Accesion Counties (PECO).

References

Jaško, V., et al., 1996: Smolník: komplexné hydrogeologické hydrochemické posúdenie ložiska Cu – Fe rúd. Aquipur Bratislava, 1-124.

Ettler, V., Baillif, P., Touray, J. C., 1999: Natural weathering of glass from Pb-metallurgical slag: a comparison with laboratory leaching tests using XPS, Bull. Liaison S.F.M.C., 11, 146-147.

Ettler, V., Piantone, P., Touray, J. C., 2001: Metallurgical slag/water interaction: experimental approach, thermodynamic modelling and long-term assesment, In: Cidu (Ed), Water-Rock Interaction, Balkema Publishers, Swets & Zeitlinger, Lisse, ISBN 90 2651 824 2.

Šottník, P., Dubíková, M., Lintnerová, O., Rojkovič, I., Šucha, V., Uhlík, P., 2002. The links between physico-chemical character of different mining waste in Slovakia and their environmental impacts, Geologica Carpathica, 53, 227-229.

Slovak Geol. Mag.,9, 2 – 3(2003), 201 – 203

Stream Sediments and Soil Pollution in the Smolník Mining Area (Slovakia)

OTÍLIA LINTNEROVÁ, PETER ŠOTTNÍK and STANISLAV ŠOLTÉS

Comenius University Bratislava, Faculty of Natural Sciences, Mlynská dolina G, 842 15 Bratislava, Slovakia,
Phone: (+421)2-60296-495, lintnerová@fns.uniba.sk, sottnik@fns.uniba.sk, soltes@fns.uniba.sk

Abstract. The Smolník is a mining area in Slovakia serious polluted by acid mine drainage (AMD). The apparent pH and metal concentration changes in stream water are observed downstream from the abandoned mine to confluence with the Hnilec River. The goal of this works is to evaluate partitioning of metals in stream sediment, water suspended solids and bank soils in polluted Smolník Stream and Hnilec River. It was documented that rapid precipitation of iron oxyhydroxides removed the dissolved metals from the water in the polluted section of the stream. Potentially toxic AMD related metals (Fe, Cu, Zn, Pb and As) are cumulated in stream sediment mainly in oxides and in organic mater fractions. Preliminary results indicated that various factors (seasonal water volume change, mineral phases in aggregates, sorption of organic and inorganic ions/ligand) might to change amount transported in suspended solids in the stream. Metals are accumulated in soil on the stream banks, however the mobile or active forms (species) of metals are increased locally in the vicinity of various mine activity related waste. Increased content of metals in the soils on the metallurgic slag sick it was documented. This and other mine waste sick could change water quality in polluted area and to the different degree impact catchment biota.

Key words: sequential extraction, heavy metals, mine pollution

Introduction

One of the aims of our research project is to analyses accumulation and spill potentially toxic metals, liberated by acid mine drainage (AMD), in sediments and soils in the Smolník Stream catchment (Fig 1). Stream (river) sediments and bank soils accumulate metals which potential toxicity could occur in various time and condition and could cause serious problems. It is important, that the main portions of liberated metals by AMD are attenuate in iron oxyhydroxides precipitated in the oxidic water mixing conditions (Lintnerová 1996, Lintnerová et al., 1999).

Location and mine history

The Smolník Mine area is situated in the SE part of the Slovenské Rudohorie Mts .The Early Palaeozoic volcanic-sedimentary chalcopyrite-pyrite deposit was mined for several centuries. Smolník Mine operated until 1990 and until 1995 it was flushed. Acid mine water rock began to outflow and pollute waters of the Smolník Stream and Hnilec River afterward. The new technical arrangements of the surface drainage systems and remediation of the mine work area lowered the mine water amount, acidity and metal concentration of mine water. The new results have shown that mine water from aban-doned and flooded mine is acid (pH 3,5 to 4,1) and total dissolved solids may have as high as 5000 mg/L (Rojkovič et al., 2002). Acid generation potential rises from high content of pyrite in the abandoned ore mine and in surrounding rock.

Monitoring, samples collection and methods

We have organized sediment, suspended solids, soils and AMD-related (ochre) precipitates quality monitoring along Smolník Stream and the Hnilec River part affected by the mine spill (Figs. 1).

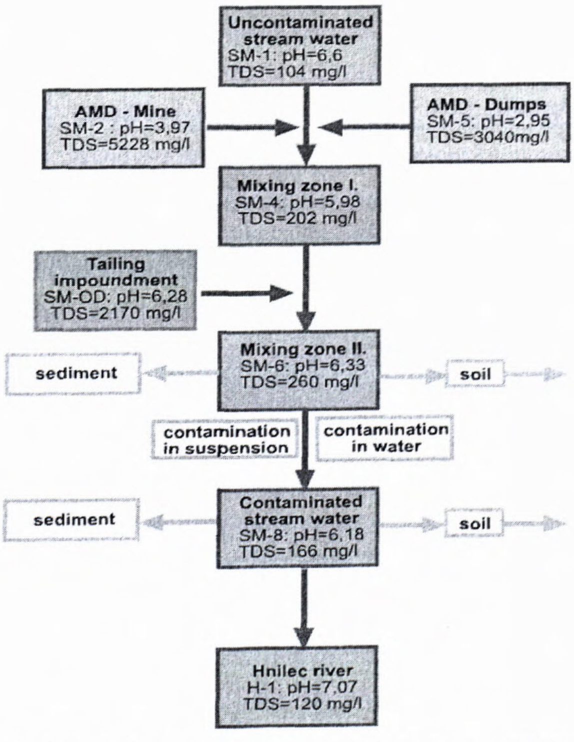


Fig. 1 Principal scheme of the main pollutants partitioning in the study area.

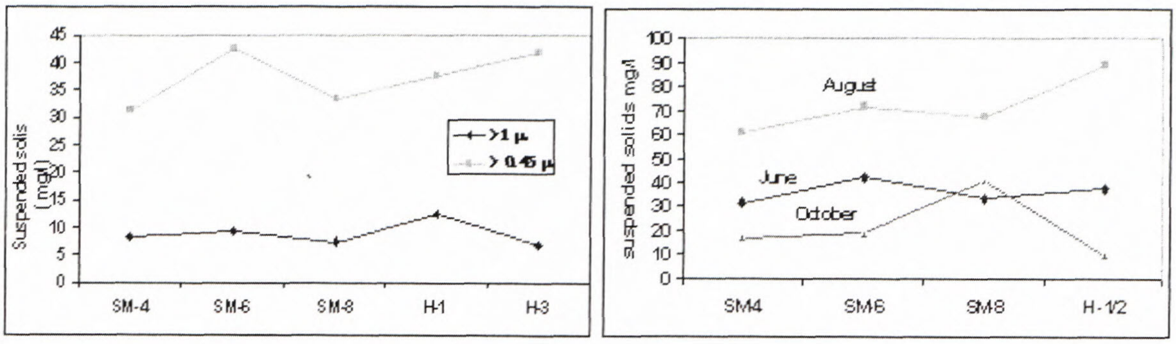


Fig.2A. The grain size fractions collected from Smolník Stream (SM-4 to SM-8) and Hnilec River (H-1, H-3), June 2002, 2B The comparison of mass of suspended solid from Smolník Stream monitoring points in tree time periods in 2002.

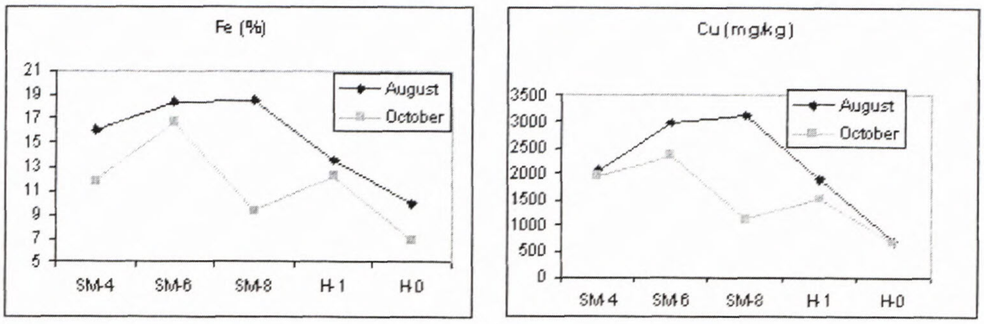


Fig. 3. Content of metals in suspension samples expressed on the (HNO_3) acid dissolved basis collected in 2002. Samples were collected during 5 days and cumulative samples were analyzed

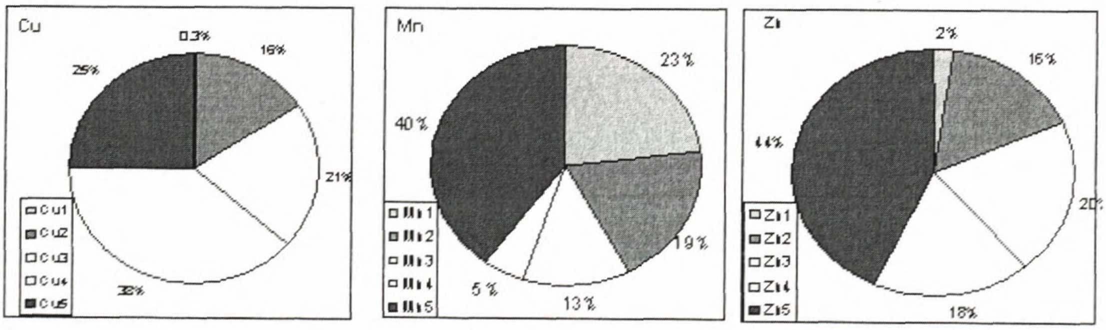


Fig. 4. Metals (Cu, Mn, Zn) distribution in the sample SM-8. Large accumulations of metals are in dissolvable (1) and exchangeable specie (2) however Cu and Zn prefer oxides (3) and in organic matter (4,respective sulfide).

The suspended solids and AMD related precipitates samples were collected in June, August and October in 2002. Two methods of collection the suspended solids were used. 1) Filtering solids from contaminated and uncontaminated stream water passed through pore size of the 0,45 μm Millipore membrane filter: 2) Collecting (~24 hours) the suspended solids by free sedimentation of large volume (100L) polluted water and by decantation of the water. Suspended solids samples were dried at 105°C to a constant mass. 0,1 or 0,5 g of sample was digested by concentrated HNO_3 for 2 hours at 95°C in a water bath. 11 elements (Fe, Mn, Al, Ca, Mg, Na, K, Cu, Zn, Pb, As) were analyzed by AAS and ICP-AES. The insoluble residue of samples was dried at 105°C to constant mass. The results were expressed as acid dissolved (HNO_3) basis metals contents.

Stream sediment and soils. Each sediment and soil sample was dry at 60°C overnight and sieved to separate < 63 μm fraction. Apart the same methods used to characterize the suspended solids, sequential extraction procedure for the speciation of seven selected elements in five stream sediments samples (Si, Al, Fe, Cu, Mn Zn, As) were performed. The modified Tessier´s and Community Bureau of Reference (BCR) extraction procedures were used (Mackových et al., 2003). Five steps extraction - water dissolvable (F1), exchangeable and bound to carbonate (F2), bound to iron and manganese oxides (F3), bound to organic matter and sulfide (F4) and residual fractions (F5) were performed and analyzed on the selected metals. Total organic carbon (TOC) content was performed by C-MAT 550 analytical system.

Tab. 1. Chemical composition of AMD related precipitates from abandoned mine (SM2), mine dumps (SM5) and tailing impoundment (SM6OD, SMOD). Tailing related precipitates are slight acid (pH 5-7, see Fig. 1) and As-rich.

Element (mg/kg)	**SM2**	**SM5**	**SM6OD**	**SMOD**	**Element (mg/kg)**	**SM2**	**SM5**	**SM6OD**	**SMOD**
Fe (%)	42.7	44.9	47.9	33.15	**Mn**	103	35	196	606
Al	10000	1203	1116	280	**Cu**	270	302	182	731
Ca	27	77	772	21031	**Zn**	77	45	155	1052
Mg	1696	616	798	3398	**Pb**	459	41	78	<0,1
Na	266	157	140.4	5237	**As**	2523	824	7680	10724
K	727	551	145.2	1978	**SO_4^{2-}**	8450	13850	8750	165

Results

Fresh precipitates are very slight crystallized and fine (in range 50-100 nm) particles coat bottom and plants and animals on the bank and bottom of the stream. AMD related iron oxyhydroxide precipitates (Tab. 1) are transported by stream in suspension (Fig.1)

It was confirmed that particles > 1µm represent minor part of the suspension (Fig 2A). The total mass of suspended solids collected from 100 l of Smolník Stream water was between 1.2 g and 7.2 g. The largest amount of suspended solids was locate in point SM8 (Fig 1, 2) The solids mass transported by stream has changed during year (Fig. 2B). The chemistry of AMD discharged from flooded mine responses to the seasonal climate fluctuation to some step in the area (Rojkovič et al 2002). Results of mineralogical and chemical analyze demonstrate that in the wet period or when increased volume of water in stream (400 to 2000 L/s) content of iron oxides decreases and content of rock minerals (quartz, mica, chlorite) intensive rise (e.g. from 20 to 70 %) in suspended solids. The concentrations of selected metals expressed on acid dissolved basis change in time too, however these changes more probably reflect the dissolved metals supply from the mine and the tailings in monitored time periods (Fig 3).

Sequential extraction procedures are connected with some problems, mainly partial selectivity, re-adsorption and release of metal during extraction steps and other. The sufficient information about mineralogical and geochemical nature of steam sediments could eliminate these potential complications. It is well known that mobility of potentially toxic metals depends on their different binding or specific chemical forms and total concentration of metals is not the most important. Metal partitioning in all phases however very important is exchangeable or bioavailable phases to assess mobility and environmental risk (Fig. 4). Rise accumulation of the metals mainly Fe, Cu, Zn, Mn, has been documented also in soils samples from the stream banks. The Fe contents in soils documented two main source of pollution, the flooded mine (SM-4) and tailing impoundment (SM-6). There had been located several types of mining and related activity wastes, for example metallurgic slag and could be a source of some metals, mainly Cu in the Smolník area.

Conclusion

1. Total concentration of studied metals in sediments increased progressively toward to the Smolník Stream and Hnilec River confluence. Total content of Fe, Cu, Zn and Mn also increased in comparison with their contents monitored in 1995 in the contaminated part of Smolník Stream.

2. The largest part of studied metals is bounded or adsorbed by oxides and by organic matter. The contents of exchangeable Fe, Cu, Zn, Mn increase mainly in the acidic condition in the sediments.

3. Acid conditions and increased content of organic matter there are two important factors, which changed the mobility and bioavailability of metals. The most acid sediment is leached (SM4) and metals (Mn, Cu, Zn) content decrease. Leaching stops in the point SM7 and the largest concentration of metals are in the point SM-8. The SM-7 sample is enriched in organic mattes (TOC 7.35 % in comparison with SM-1: 3,5 %) Organic matter could change redox condition and metal mobility in water and abilities of iron oxyhydroxides attenuate metals.

4. Only low mobility As there are presented. The As content in the oxide fraction of stream sediments is relatively low and prevailing part of As is bound into residual fraction in sediment.

Acknowledgements

Work was supported by Slovak Ministry of Education, JRC Institute for Environment and Sustainability Ispra, Varese and Slovak Science Grant Agency VEGA (Grant project No. 1/0010/03). Project „Physico-Chemical Properties and Environmental Impact of mining waste of Slovakia“ is one part of project „Environmental Impact of Toxic Mining Wastes in Pre-Accession Countries (PECO)“.

References

Lintnerová, O., 1996: Mineralogy of Fe-ochre deposits formed from acid mine water in the Smolnik mine (Slovakia). Geologica Carpathica Clays, 5, 55-63.

Lintnerová, O., Šucha, V, Streško, V. 1999: Mineralogy and geochemistry of acid mine Fe precipitates from the main Slovak mining regions: Geologica Carpathica 50, 395-4041.

Mackových, D., Lučivjanský, P., Nováková, J., Šoltýsová, H., 2003: Some specific species of toxic elements determination using sequential extraction Book of conference proceedings: River and lake sediments. Bratislava 2003, 270-275, (in Slovak).

Rojkovič, I., Lintnerová, O., Šottník, P., Banásová, V., Šoltés, S., Uhlík, P., 2003: Physico-Chemical Properties and Environmental Impact of mining waste of Slovakia Administrative report, Comenius University Bratislava, 77 pp (in Slovak).

Instructions for authors

Slovak Geological Magazine – periodical of the Geological Survey of Slovak Republic is quarterly presenting the results of investigation and researches in wide range of topics: regional geology and geological maps, lithology and stratigraphy, petrology and mineralogy, paleontology, geochemistry and isotope geology, geophysics and deep structure, geology of deposits and metallogeny, tectonics and structural geology, hydrogeology and geothermal energy, environmental geochemistry, engineering geology and geotechnology, geological factors of the environment, petroarcheology.

The journal is focused on problems of the Alpine-Carpathian-Balkan region

General instructions

The Editorial Board of the Geological Survey of Slovak Republic – Dionýz Štúr Publishers accepts manuscripts in correct English. The papers that do not have sufficient accuracy in language level will be submitted back for language correction.

The manuscript should be addressed to the Chief Editor or the Managing Editor.

Contact address:

Geological Survey of Slovak Republic – Dionýz Štúr Publishers,
Mlynská dolina 1, 817 04 Bratislava, Slovak Republic
e-mail addresses: hok@gssr.sk
gabina@gssr.sk
http://www:gssr.sk

The Editorial Board accepts or refuses a manuscript with regard to the reviewer's opinion. The author is informed of the refusal within 14 days from the decision of the Editorial Board. Accepted manuscript is prepared for publication in an appropriate issue of the Magazine. The author(s) and the publishers enter a contract establishing the rights and duties of both parties during editorial preparation and printing, until the time of publishing of the paper.

Text layout

The manuscript should be arranged as follows: TITLE OF THE PAPER, FULL NAME OF THE AUTHOR(S); NUMBER OF SUPPLEMENTS (in brackets below the title, e.g. 5 figs., 4 tabs.), ABSTRACT (max. 30 lines presenting principal results) – KEY WORDS – INTRODUCTION – TEXT – CONCLUSION – ACKNOWLEDGEMENTS – APPENDIX – REFERENCES – TABLE AND FIGURE CAPTIONS – TABLES – FIGURES. The editorial board recommends to show a localisation scheme at the beginning of the article.

The title should be as short as possible, but informative, compendious and concise. In a footnote on the first page, name of the author(s), as well as his (their) professional or private address.

The text of the paper should be logically divided. For the purpose of typography, the author may use a hierarchic division of chapters and sub-chapters, using numbers with their titles. The editorial board reserves the right to adjust the type according to generally accepted rules even if the author has not done this.

Names of cited authors in the text are written without first names or initials (e.g. Štúr, 1868), the names of co-authors are divided (e.g. Andrusov & Bystricky, 1973). The name(s) is followed by a comma before the publication year. If there are more authors, the first one, or the first two only are cited, adding et al. and publication year.

Mathematical and physical symbols of units, such as %, ‰, °C should be preceded by a space, e.g. 60 %, 105 °C etc. Abbreviations of the units such as second, litre etc. should be written with a gap. Only SI units are accepted. Points of the compass may be substituted by the abbreviations E, W, NW, SSE etc. Brackets (parentheses) are to be indicated as should be printed, i.e. square brackets, parentheses or compound. Dashes should be typed as double hyphens.

If a manuscript is typed, 2 copies are required, including figures. The author should mark those parts of a text that should be printed in different type with a vertical line on the left side of the manuscript. Paragraphs are marked with 1 tab space from the left margin, or by a typographic symbol. Words to be emphasized, physical symbols and Greek letters to be set in other type (e.g. *italics*) should be marked. Greek letters have to be written in the margin in full (e.g. *sigma*). Hyphens should be carefully distinguished from dashes.

Tables and figures

Tables will be accepted in a size of up to A4, numbered in the same way as in a text.

Tables should be typed on separate sheets of the same size as text, with normal type. The author is asked to mark in the text where the table should be inserted. Short explanations attached to a table should be included on the same sheet. If the text is longer, it should be typed on a separate sheet.

Figures should be presented in black-and-white, in exceptional cases also in colour which must be paid approx. 100 EUR per 1 side A 4. Figures are to be presented by the author simultaneously with the text of the paper, in two copies, or on a diskette + one hard copy. Graphs, sketches, profiles and maps must be always drawn separately. High-quality copies are accepted as well. Captions should be typed outside the figure. The graphic supplements should be numbered on the reverse side, along with the orientation of the figures. Large-size supplements are accepted only exceptionally. Photographs intended for publishing should be sharp, contrast, on shiny paper. High quality colour photographs will only be accepted depending on the judgement of the technical editors.

If a picture is delivered in a digital form, the following formats will be accepted: *.cdr, *.dxf, *.bmp, *.tiff, *.wpg, *.fga., *.jpg *.gif, *.pcx. Other formats are to be consulted with the editors.

References

Should be listed in alphabetical and chronological order **according to annotation in the text** and consist of all references cited.

Standard form is as follows: 1. Family name and initials of author(s), 2. Publication year, 3. Title of paper, 4. Editor(s), 5. Title of proceedings, 6. Publishers or Publishing house and place of publishing, 7. Unpublished report – manuscript should be denoted MS. Unpublished paper can appear as personal communications only. 8. Page range

Quotations of papers published in non-Latin alphabet or in languages other than English, French, Italian, Spain or German ought to be translated into English with an indication of the original language in parentheses, e.g.: (in Slovak).

Example:

Andrusov, D., Bystrický, J. & Fusán, O., 1973: *Outline of the Structure of the West Carpathians.* Guide-book for geol. exc. of Xth Congr. CBGA. Bratislava: Geol. Úst. D. Štúra, 44 p.

Beránek, B., Leško, B. & Mayerová, M., 1979: Interpretation of seismic measurements along the trans-Carpathian profile K III. In: Babuška, V. & Plančár, J. (Eds.): *Geodynamic investigations in Czecho-Slovakia.* Bratislava: VEDA, p. 201-205.

Lucido, O., 1993: A new theory of the Earth's continental crust: The colloidal origin. *Geol. Carpathica,* vol. 44, no. 2, p. 67-74.

Pitoňák, P. & Spišiak, J., 1989: Mineralogy, petrology and geochemistry of the main rock types of the crystalline complex of the Nízke Tatry Mts. MS – Archiv GS SR, Bratislava, 232 p. (in Slovak).

Proofs

The translator as well as the author(s) are obliged to correct the errors which are due to typing and technical arrangements. The first proofs are sent to author(s) as well as to the translator. The second proof is provided only to the editorial office. It will be sent to authors upon request.

The proofs must be marked clearly and intelligibly, to avoid further errors and doubts. Common typographic symbols are to be used, the list and meaning of which will be provided by the editorial office. Each used symbol must also appear on the margin of the text, if possible on the same line where the error occurred. The deadlines and conditions for proof-reading shall be stated in the contract.

Final remarks

These instructions are obligatory to all authors. Exceptions may be permitted by the Editorial Board or the managing editor. Manuscripts not complying with these instructions shall be returned to the authors.

1. Editorial Board reserves the right to publish preferentially invited manuscript and to assemble thematic volumes,
2. Sessions of Editorial Board – four times a year and closing dates for individual volumes will be on every last day of March, June, September and December.
3. To refer to one Magazine please use the following abbreviations: *Slovak Geol. Mag.,* vol. xx, no. xx. Bratislava: D. Štúr. Publ. ISSN 1335-096X.

Indexed/Abstracted in: Chemical Abstracts, Ulrich´ s International Periodical