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 (Medved' 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 (Medved' 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.