

Determinations of minor and major elements in stream sediments for geochemical mapping

Daniela Mackových*, Hana Mjartanová*, Pavol Lučivjanský*

Determinations of minor and major elements in stream sediments were performed by total decomposition (sintering or digestion) of sample with a mixture of mineral acids, or by non-destructive technique (pressing pellets).

In order to determine the elements, atomic absorption spectrometry (AAS) for As, Sb, Se, Bi, Hg, Tl; atomic emission spectrometry with inductively coupled plasma (ICP-AES) for Al, B, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Ti, V, W, Zn; optical emission spectrometry (OES) for Sn, and X-ray fluorescence spectrometry (XRF) for Ba, Ga, Rb, Sr, Y, Zr were used.

Key words: mapping, geochemical maps, stream sediments, sample preparation, major element analysis, minor element analysis, spectroscopy, Slovakia

Introduction

At present, the protection of the environment is one of the most important global problems. A huge economical development has had a negative influence on our environment in the last decades.

Heavy metals that infiltrate into groundwater, as well as soil and stream sediments including those from anthropogenic sources represent a serious danger to all living organisms.

The stream sediments consists of geologic, anthropogenic and biological components. There are formed from colloids (suspended solids) or dissolved chemicals. The sediments are also conveyers of heavy metals.

The project entitled: *Investigations of the geological factors of the environment*, co-ordinated by the Geological Survey of Slovak Republic, has belonged to the most important ones regarding environmental monitoring.

The principal objectives of the project were:

1) to compile *Geochemical Atlas of the Slovak Republic*, scale 1 : 1,000,000 (1991/1995) together with maps of accompanying geochemical and ecological features, scale 1 : 200,000. It was implemented by assessing the concentrations and the distribution pattern of 35 chemical elements in stream sediments, soils, groundwater and forest biomass. In stream sediments the elements were analysed in Geoanalytical Laboratories in Spišská Nová Ves,

2) to make maps representing geological factors of the environment of the Slovakia, regional ecological maps 1 : 50,000 were used.

Sample preparation

The active stream sediments represented the basic sample medium. Samples of 1,5–3 kg each were collected using a grid pattern: 1 sample per 2 km². Samples were dried at 40°C, crushed by hand and sieved through 0.125 mm mesh. A part of sample was milled in an agate mill to reach a 0.06 mm fraction after quartering. All procedures were done without contact with metals.

Chemical analysis

Many authors have worked on methods concerning the decomposition of geological materials (Jeffer, 1975; Weiss at al., 1983; Doležal et al., 1966; Medved' et al., 1992; Bakhtar et al., 1989; Derie, 1984; Butler & Smith, 1988; Krakovská & Mackových, 1996a). The techniques connected with transferring of solids to solutions represent a very important factor that affects both the efficiency and the reliability of analytical procedures.

The determinations of minor and major elements in stream sediments were performed by a total decomposition of samples with sintering or digestion with a mixture of mineral acids and by non-destructive technique from pressed pellets.

Besides, the inorganic components of stream sediments contain an organic material too (up to 20%). Insufficiently decomposed organic materials could have a negative influence on their determinations. That was the main reason why samples were ignited during an hour at a temperature of 580°C, or decomposed with H₂O₂. After removing the organic matter, the remaining inorganic matrix was decomposed. The choice of the suitable decomposition method of solid materials is important, because it is a source of errors.

To determine the elements, atomic absorption spectrometry (AAS) for As, Bi, Hg, Sb, Se, Tl; atomic emission spectrometry with inductively coupled plasma (ICP-AES) for Al, B, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Ti, V, W, Zn; optical emission spectrometry (OES) for Sn; and X-ray fluorescence spectrometry (XRF) for Ba, Ga, Rb, Sr, Y, Zr were used. The limits of detection for the determined elements in stream sediments are listed in tab. 1.

A. Determination of Al, Ca, Fe, Mg, Mn, Ti

Stream sediment samples were decomposed by sintering with Na₂O₂ in a platinum crucible at a temperature of 490°C during 30 minutes (Jeffer, 1975; Doležal et al., 1966). After sintering and cooling down the sample was dissolved with HCl (1+1). The content of elements was determined by a ICP-AES using a simultaneous spectrometer ARL 34,000. The used reagents were of p.a. purity. There were also used for blank experiments in each series of samples.

In order to reduce physical interferences from spraying samples of the high level of dissolved material, transport of

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

Tab. 1. Limit of detection for determined elements in stream sediments

Element	Limit of detection	Element	Limit of detection
Al	0.01%	Mn	0.001%
As	0.1 ppm	Mo	0.2 ppm
B	5 ppm	Na	0.01%
Ba	30.0 ppm	Ni	1.0 ppm
Be	0.1 ppm	P	0.01%
Bi	0.1 ppm	Pb	5 ppm
Ca	0.01%	Sb	0.1 ppm
Cd	0.1 ppm	Se	0.1 ppm
Ce	10 ppm	Sn	1 ppm
Co	1.0 ppm	Sr	5 ppm
Cr	5 ppm	Ti	0.001%
Cu	1 ppm	Tl	0.2 ppm
Fe	0.01%	V	5 ppm
Ga	5 ppm	W	5 ppm
Hg	0.03 ppm	Y	5 ppm
K	0.01%	Zn	1 ppm
Li	1 ppm	Zr	5 ppm
Mg	0.01%		

sample, etc., a Cd internal standard was used. Both the short- and the long-term reproducibility was improved. The analytical signal was evaluated using a calibration curve. The calibration curve was plotted from 7 mixed calibration standard solutions and a blank solution. The calibration and sample solutions were prepared under the same conditions.

The precision and accuracy of determinations were tested on China certified reference materials of stream sediments GBW 07 309, 07 310, 07 312.

The precision of analytical results is expressed by a relative standard deviation (RSD) from n measurements. (n>30). The accuracy was tested by comparing of certified and experimented values.

B. Determination of Ce, K, Li, Na, P

All the elements were determined after decomposition of 0.5 g samples with a mixture of HF and HClO₄ (10+1) acids (Jeffer, 1975; Weiss at al., 1983; Doležal et al., 1966). After repeated heating of acids, a saturated solution of H₃BO₃ was added. The solution was evaporated and dissolved with HNO₃ (1+1). The solution was placed in a 50 ml volumetric flask. The contents of Ce, K, Li, Na, P were determined from this solution by a ICP-AES method using Liberty 200, Varian.

C. Determination of B, Be, Cr, V, W

These metals were decomposed by sintering with sodium peroxide at a temperature of 490°C for an hour (Jeffer, 1975; Doležal et al., 1966). The sintered material was dissolved in distilled water. The contents of elements were determined by ICP-AES Liberty 200, Varian.

D. Determination of Cd, Co, Cu, Ni, Pb, Zn

The determinations of these elements in stream sediments were performed in a Teflon crucible using a mixture of HF and HClO₄ (Jeffer, 1975; Weiss at al., 1983; Doležal et al., 1966). After repeated evaporation with HF, the ob-

tained residue was dissolved in HNO₃ (1+1) under warm conditions. After evaporating of acids, the solution was quantitatively put into a 50 ml volumetric flask. An ICP-AES method was used for determination of these elements.

E. Determination of Mo

Molybdenum was determined after sample decomposition by a mixture of mineral acids. The sample (1 g) was digested in the mixture of HCl and HNO₃, (3+1). After precipitation of the solution in a sand bath, 3 ml of H₂SO₄ (1+1) was added. The obtained residue was dissolved and put into a 50 ml volumetric flask using 0,5 M HCl. Molybdenum was extracted into MIBK and after evaporation of the solvent the remaining precipitate was dissolved in HNO₃ (1+1) under warm conditions. Then the solution was quantitatively placed in a volumetric flask. The element was determined by AES-ICP Liberty 200, Varian with an ultrasonic Nebulizer, Cetac.

F. Determination of As, Bi, Sb, Se

The sediment sample was digested in a mixture of HCl and HNO₃ (3+1) after removing organic substances by H₂O₂ (Krakovská & Mackových, 1995, 1996a, b). The remaining portion of HNO₃ was removed by adding aqueous solution of urea. These elements were determined by AAS with hydride generation. Arsenic and Antimony hydrides were generated after preliminary reduction of As⁵⁺ and Sb⁵⁺ into As³⁺ and Sb³⁺ with an aqueous solution of KI. Selenium and bismuth hydrides were generated straight from 3M HCl.

G. Determination of Ba, Ga, Rb, Sr, Y, Zr

For determinations of these elements, an X-ray fluorescence method was used. 5 g of homogeneous sample was mixed with 1 g of Hoechst wax and pressed into a 40 mm diameter pill under a pressure of 250 MPa. The amounts of different elements were determined using a set of calibration standards. In an X-ray fluorescence method, the intensity of a particular line (count rate) is influenced by other elements of a matrix. To eliminate these influences a Yong model was used with mathematical elimination of interferences. The signal was integrated from a calibration line.

H. Determination of Tl

The stream sediment sample was decomposed in Pt crucible with a mixture of HNO₃ and HF (1+2) and evaporated to fumes (Jeffer, 1975). The evaporation was repeated with HF, HF and HClO₄ (2+1) and twice with HBr enriched by Br. The precipitated residue was dissolved in 0.1 M HBr. Thallium was extracted into MIBK and determined with AAS with electrothermal atomisation using peak high absorbance measurement.

J. Determination of Sn

A total of 0.1 g sample was mixed with 0.1 g of a spectral additive (Li₂CO₃ and C) and exposed on a photographic plate. To reach better accuracy of results, an internal standard — Ge was used. Optical density was evaluated by a calibration curve method using microdensitometer.

K. Determination of Hg

Mercury was determined with AMA — 254 (single — purpose analyser). Determination is based on thermo-oxidised decomposition of a solution and on absorption of mercury vapours on an amalgamator. Then the experiment

element was released by heating, and its vapours were directed by an oxygen stream into the measuring cell. The absorption signal was evaluated with a calibration curve method.

Quality assurance

In total, 25,000 samples of all the area of the Slovak Republic were analysed. The processing of such a large of samples posed high demands on quality of analytical data. Certified reference materials (China — GBW), internal reference materials analysed in 3 or 4 laboratories, then internal and external control samples and repeated digestion of samples were used. The number of controlled analyses was ranged 15 to 20%. The reference material (RM) was analysed with every series of samples. Based on the result of RM analyses, regulation charts were constructed. With co-operation of the Slovak Metrological Institute, the authors of the project prepared two reference materials of stream sediments — Telgart and Voznica. They correspond to international standards.

Based on the results of stream sediments analyses, a set of geochemical maps have been made. They will be used for assessment of environmental contamination in the future. They will surely have a significance from the international point of view, as they will allow us to assess the pollution of the area of Slovakia.

Conclusions

Various optimal decomposition procedures for determination of selected elements in stream sediment samples have been applied. Both the conventional and the sintering decomposition procedures for determination of particular element groups have been presented in a detail. They provide reliable results, which has been confirmed by the analyses performed for certified reference materials.

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