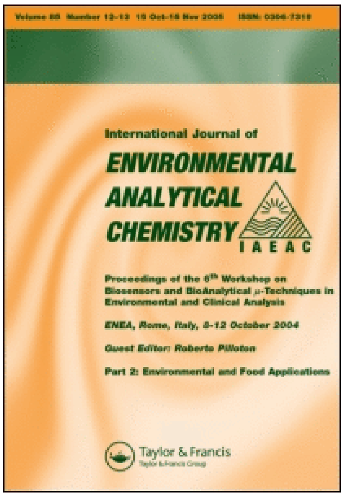

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THE INFLUENCE OF EXPERIMENTAL LEACHING CONDITIONS FOR THE DETERMINATION OF THE SOLUBLE ELEMENT CONTENT OF SOIL AND STREAM SEDIMENT SAMPLES

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The Hungarian Geological Survey – Geological Institute of Hungary participated in an INCO-Copernicus project which was aimed at the harmonisation of analytical methods and finished recently. In the first phase, participating geological laboratories entered the International Soil Exchange (ISE) scheme. Laboratories determined total and leachable element contents of soil (and stream sediment) samples, using their own methods. This article in intended to summarise the problems and conclusions regarding the determination of leachable (mobile) elements. Using their own methodologies, laboratories obtained fairly divergent results, especially for some elements. In order to eliminate the variance originating from applying different methodology, a standardised common method was designed for aqua regia leaching. The spread of the results did not improve significantly because of the insufficient control of the applied open vessel method. The final conclusion was: in order to produce internationally comparable results, the use of well-defined and well-controllable digestion methods is strongly recommended. A typical example might be the use of the microwave assisted digestion methods for all geological institutes participating in international geochemical programmes.

Keywords: Soil; Aqua regia digestion; Leaching efficiency; Method harmonisation

INTRODUCTION

The Hungarian Geological Survey – Geological Institute of Hungary (MAFI) was a participant of the INCO-Copernicus project titled “Development of Analytical Procedures to Guarantee Quality Assurance in International Environmental Monitoring”. This project lasted for 3 years and finished recently. Participating institutes were the geological institutes and surveys of following countries: The Netherlands, Finland, United Kingdom, Hungary, Poland, Czech Republic, Slovak Republic, Russia, Estonia, Lithuania and Romania.

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The aim of the project was to harmonise analytical methods, applied at the laboratories of the geological institutes of the participating 11 countries in order to obtain internationally comparable and mutually acceptable analytical results in the course of geochemical projects because geochemical phenomena do not stop at country borders. Nowadays, there is more and more urgent need to create a consistent, internationally comparable geochemical database. Among others, determination of the reliable geochemical background is of major importance.

The INCO project was designed like a proficiency testing exercise. Thus the most important aspect was to assess the spread of results, both within individual laboratories and between laboratories, and then secondly to estimate the bias. In the first phase, this project involved the participation in the International Soil Exchange (ISE) scheme run by Wageningen Agricultural University in the Netherlands. The idea was to use this pre-existing proficiency testing scheme in order to identify weak points and problem areas of the methodology of each participant. This inter-laboratory exercise could be utilised by the participating laboratories when setting up the quality assurance systems and applying for accreditation.

The WEPAL ISE (Wageningen Evaluating Programmes for Analytical Laboratories – International Soil Exchange) scheme consists of four analytical periods each year. It means that round robin samples are distributed every three months [1]. Participating laboratories of the INCO-Copernicus project received sets of four samples during each round in the 1997.3 to 1999.3 periods (9 periods in total). Data evaluation for the INCO project was independently made by the Geological Survey of Finland [2]. (Evaluation is detailed elsewhere [3–5].) The so-called monitoring sample (Code No. 921-M) was included into each run.

During the ISE scheme both total element contents of the soil samples ("real total" content) and element contents leached by aqua regia ("so-called total" content) were determined. Determination of total ("real total") element contents was carried out after total decomposition (by destruction of silicate lattice) or analysing solid samples (e.g., by XRF spectrometry). Determination of "so-called total" concentrations was performed after aqua regia digestion. In the latter case, for some elements total or almost total dissolultion could be obtained, while some other elements remained partly insoluble.

Originally it was recommended that laboratories should analyse the samples using their normal, routinely used analytical methods and restrict themselves to one method for total metals and one for leachable metals. So, participant laboratories used very different analytical methods, probably with very different efficiencies.

Determination of total element contents (in general) did not cause significant problems. Analytical results were generally in good agreement with the consensus concentration values (i.e., the ISE median values). Our experiences about the determination of total element contents are discussed elsewhere [3–5]. This article is intended to summarise problems and conclusions to be drawn regarding the determination of leachable (mobile) elements (or using ISE terminology: "so-called total" element contents).

It might be worth to make a little detour regarding leachable element contents. Large-scale geochemical exploration projects usually require the determination of total element contents. For example, in the recommendations for the preparation of the global geochemical database program [6] it is explicitly mentioned that the determination of total element contents is required and the use of different partial leaching methods is considered definitely undesirable as there are numerous versions of these methods in the different laboratories and they are very difficult to standardise.

Leaching procedures applied in geochemical and environmental research can be classified into four main groups: (the leaching agent can be nitric acid, aqua regia or other)

- leaching in closed system, at high pressure (possibly in a microwave digestion unit) (this method seems to be the least problematic one, having the best efficiency and being the best controllable; while operation with the microwave digestion unit might be time-consuming when routine analysis of a large number of samples is necessary)
- leaching in open vessel, with reflux (boiling usually at least for half an hour) (loss of volatile elements is minimised)
- leaching in open vessel, without reflux (heating or boiling for a certain time, mostly on a water bath)
- leaching in open vessel, including a controlled evaporation step (on a water bath or sand bath, possibly on hot plate)

There exist further versions, of course.

These methods are in widespread use in geological institutes beside the total decomposition methods. The element contents obtained after a strong acidic leaching can be considered as the maximum dissolved concentration values under extreme weathering conditions (e.g., highly acidic rain and long contact time).

As it was mentioned above, there are a number of elements (refractory elements – Al, Si, K, Ti, Na, Ba, V, Cr etc.) which remain partly insoluble even after a strong acidic attack (carried out under elevated temperature and pressure) because these elements are built into the silicate lattice structure of the soil or sediment sample. Other elements, namely chalcophile and some toxic elements which are the most interesting in environmental studies, (being elements of known toxicity), dissolved completely or almost completely using these methods. Use of the acidic leaching is important in the geochemical research, because the leached part of the total concentration will most likely reflect the degree of mineralisation of geochemical contrasts for mineral exploration [7–10].

In the majority of geological institutes, mainly because of work organisation aspects, analysis of batches of numerous samples is carried out generally after acidic digestion performed in open vessel at atmospheric pressure.

On the other hand, a number of agrochemical laboratories, participating in the ISE scheme, used a microwave digestion unit (according to the mandatory standards). The median calculated from all the results of the ISE scheme was determined by the larger number of laboratories using this closed vessel decomposition technique.

EXPERIMENTAL

In this section the instrumentation and experimental conditions used in our institute (Hungarian Geological Survey – Geological Institute of Hungary) are described.

Instrumentation

Microwave assisted decompositions were carried out by a microwave digestion system made by Milestone S.r.l. (Sorisole, Italy), type: MEGA MLS 1200 with an

TABLE I Details of microwave assisted aqua regia digestion programme

Time (min)	*Power* (W)
2	250
2	0
5	250
5	400
5	500
2	Ventilation

TABLE II Operating parameters of the ICP-OES instrument

RF power	1000 W
Reflected power	< 10 W
Plasma gas flow rate	12 L/min
Sheath gas flow rate	0.2 L/min
Nebuliser type	Cross-flow
Nebuliser flow rate	0.4 L/min
Nebuliser pressure	2.7 bar
Observation height	15 mm (above load coil)

MDR-100/6/100/110 rotor (high pressure system, allowing maximum 110 bar internal pressure). Digestion vessels were made of TFM fluoropolymer provided with a protection shield made of special HTC material. Details of the decomposition program are listed in Table I.

The ICP-OES spectrometer used for the determination of the majority of the elements was a Jobin Yvon (Longjumeau, France) JY70 combined (simultaneous-sequential) instrument. Instrumental operating conditions are listed in Table II.

Spectral lines chosen for the determinations are listed in Table III.

Arsenic and antimony were determined after decomposition, by Hydride Generation AAS, using a Varian (Mulgrave, Victoria, Australia) SpectrAA-10BQ instrument with a HG-2 hydride generation unit (made by Labtech, Brno, Czech Republic).

Operating conditions are listed in Table IV.

Chemicals and Reagents

High purity distilled, de-ionised water was used throughout the work (Purite HP Still Plus reverse osmosis system). Hydrochloric acid 36% and nitric acid 70% used for digestion were BDH (Poole, UK) products, 'SpectrosoL' quality. Sodium borohydride, sodium hydroxide, potassium iodide and ascorbic acid, used for the determination of hydride forming elements, all were analytical reagent grade.

The stock solution for calibration standards was a mixed solution containing 23 elements (1000 mg L^{-1} each) and was from Merk (Merck ICP-Multi-element standard solution IV). Analytical standard solutions were made up by dilution of this stock solution. Vanadium was not present in this solution, so it was added to the calibration standard solutions using a single element standard solution (V standard solution, 1000 mg L^{-1}, 'SpectrosoL' grade from BDH).

TABLE III Analytical program for ICP-OES determination of "so-called total" elements

Element	*Wavelength* (nm)	*Background* (nm)	*Det. lim. in solids* (mg/kg) (3σ)
Mo	202.030 m	−0.0295	1
Cr	205.552 p	+0.0635	2
P	213.618 m	−0.0441	200
Zn	213.856 p	+0.0635	1
Pb	220.353 m	+0.0206 −0.0235	5
Co	228.616 p	−0.0635	2
Cd	228.802 m	+0.0586	1
Ni	231.604 p	+0.0635	2
Ba	233.527 p	+0.0635	0.5
Mn	257.610 p	+0.1143	100
Fe	259.940 p	+0.0635	500
Mg	279.080 p	+0.0635 −0.0635	500
Al	308.215 p	+0.0635	500
V	311.071 m	+0.039	2.5
Ca	317.933 p	−0.0635	500
Cu	324.754 p	−0.0635	0.5
Ti	334.940 p	−0.0847	20
Sr	407.771 p	+0.0635	1
Na	589.592 m	+0.0428	200
Li	670.784 m	−0.0595	0.5
K	769.896 m	−0.0447	200

m = using monochromator; p = using polychromator.

TABLE IV "So-called total" elements determined by hydride generation atomic absorption spectrophotometry

	As	*Sb*
Lamp current (mA)	5	10
Observation height (mm)	16	16
Delay time (s)	40	40
Measurement time (s)	3	3
Background correction	none	none
Wavelength (nm)	197.26	206.83
Slit width (nm)	1.0	0.5
Flame	air–acetylene	air–acetylene
Acetylene flow rate (L/min)	1.5–2.0	1.5–2.0
Acetylene pressure (bar)	0.6	0.6
Argon pressure (bar)	2.8	2.8
Argon flow rate ("digit")	80	80
Sample flow rate (mL/min)	11	11
1% $NaBH_4$ flow rate (mL/min)	2.5	2.5
Detection limit in rock (mg/kg)	0.5	0.5
KI solution concentration (%)	20	20
Ascorbic acid solution concentration (%)	10	10

In the atomic absorption spectrometric determinations (determination of arsenic and antimony), calibration standards were made using single element standard solutions (As and Sb standard solutions, both $1000\,\mathrm{mg\,L^{-1}}$, 'SpectrosoL' grade from BDH).

Sample Preparation Procedures

All of samples were received from the WEPAL ISE scheme.

According to the WEPAL ISE scheme, most samples which were distributed were dried at 40°C in ovens in which the moist air was driven out. All samples were next milled. Larger clods were first broken to particles of about 2 mm using a Retsch Jaw crusher. Next the samples were milled using a Retsch Cross-Beater mill till a fraction smaller than 0.5 mm. The samples were next subdivided using the automatic equipment of WEPAL. To get homogeneous subsamples WEPAL constructed special sample dividers one for bulk samples and one for further division of the bulk samples into smaller units [11,12].

According to the original design of the INCO-Copernicus project it was recommended that laboratories should analyse the samples using their normal, routinely used analytical methods and restrict themselves to one method for total metals and one for leachable metals. So, participant laboratories used very different analytical methods, probably with very different efficiencies.

In Table V, a short compilation of the applied leaching methods is shown. These methods were used by the participants of the INCO-Copernicus project for the determination of the "so-called total" element contents. Laboratories are marked with their ISE laboratory code.

Two of the eleven participants determined the total element contents only. The other nine laboratories (presented in Table V) used rather various recipes. Also the leaching agent was different, concentrated aqua regia, diluted aqua regia, "reversed aqua regia", diluted nitric acid etc. Applied method were: microwave assisted digestion in closed system, open vessel leachng at atmospheric pressure, with or without an evaporation step, with or without reflux, with boiling or heating only, or using an ultrasonic bath.

TABLE V Comparison of leaching methods used in the INCO participant laboratories

Laboratory code	*Method*	*Sample weight* (g)	*Reagent*	*Temperature*	*Time*
GAL	Open	1	20 mL cc. AR	90°C	1 h
MAFI	Open	0.25	3.8 mL cc. HCl + 1.2 mL cc. HNO_3	Evaporation on water bath	
VICTORY	Open	1	10 mL cc. AR	Boiling	5 min
TYRKEY	Open	0.5	5 mL cc. HCl + 15 mL cc. HNO_3	Boiling	2–3 min
HSIGLTLABA	Open	1	20 mL cc. AR	Evaporation on hot plate (max. 180–200°C)	
GEOPRA	Open	1	10 mL mixture ($HCl : HNO_3 : H_2O = 9 : 1 : 10$)	Room temperature overnight 30 min boiling (under reflux)	
ESPOO	Open	1.5	12 mL diluted AR ($AR : H_2O = 1 : 5$)	90°C	1 h
RGDGEOCHEM	Open	0.4	40 mL 4.5% HNO_3	Ultrasonic bath (max. 35°C)	90 min
ANALGEO	Closed microwave	1	8 mL cc. AR	CEM microwave decomposition unit	

AR = aqua regia.

Note: Laboratory JMCK did not use an own leaching method during the run of the whole project, they produced only "real total" element concentration data. They determined "so-called total" element concentrations during the "Warsaw" experiment only.

In the following section, aqua regia digestion procedures used in the Hungarian Geological Survey – Geological Institute of Hungary (MAFI) are described.

Since total decomposition and our experiences regarding that procedure, are not subject of this article, details can be found elsewhere [3].

Our methods used for the determination of "so-called total" elements were as follows. Before digestion, samples were dried at 105°C in an electric drying oven.

Open vessel leaching by aqua regia at atmospheric pressure for the determination of the "so-called total" element contents (method used in the MAFI). In our routine analysis, this method is generally used because it is suitable for handling large number of samples. Throughout the INCO-Copernicus project, this method was used for the determination of "so-called total" concentrations.

0.25 g of samples were weighed into 150 mL glass beakers. A mixture of 3.8 mL of cc. HCl and 1.2 mL or cc. HNO_3 was added. Samples were heated on a water bath until evaporation. The residue was dissolved by 3 mL of 1 : 1 HCl. The solution was filtered, transferred into volumetric flask and made up to 50 mL. Final solutions were stored in plastic bottles.

The elements determined (by our laboratory) after this decomposition method were: Cr, P, Zn, Pb, Co, Cd, Ni, Ba, Mn, Fe, Mg, Al, V, Ca, Cu, Sr, Na, K (by ICP-OES) and As, Sb (by HG-AAS). A wide set of the elements to be determined was given by the ISE scheme and participants were free to decide which elements to analyse, both after using "real total" decomposition methods and after "so-called total" decomposition. So, there were some elements which were analysed by all the participating laboratories of the INCO-Copernicus project, while other elements were analysed by a few participating laboratories only.

Leaching by aqua regia in a microwave decomposition unit (method used in the MAFI) This method is used for special tasks only because it is not as productive as the open vessel method (when we have to analyse a large number of samples routinely). The recipe was adopted from the recommendations of a round robin test organised for sewage sludge analysis, by CEN (European Committee for Standardisation), Italy. During the INCO-Copernicus project, this method was used only for control measurements.

0.5 g of samples were weighed into the digestion vessels. 6 mL of concentrated HCl and 2 mL of concentrated HNO_3 was added. The vessels were closed, placed into the rotor body and the digestion program was started. After finishing the digestion, the vessels were cooled down and opened. The solutions were filtered into volumetric flasks and made up to 100 mL with de-ionised water. Final solutions were stored in plastic bottles. This decomposition method was used to test the difference of the efficiencies of the open vessel decomposition method and the closed vessel (microwave) methods. The group of the analyte elements was selected to contain elements with different leaching characteristics. Elements were: Cr, Zn, Ni, Ba, Mn, Mg, Al, Cu, Ti, Sr, As, Mo, P, Pb, Co, Cd, Fe, V, Ca, Na, Li, K.

In the course of the INCO project, a standardised common aqua regia leaching method was designed and applied by all of the participants (details are described later), called "Warsaw method".

"Warsaw" aqua regia leaching method was agreed as follows: 1 g of sample was weighed into a 150 mL glass beaker (tall form, approximately 6 cm in diameter and 10–12 cm tall).

15 mL of AR grade concentrated aqua regia (3 : 1 HCl : HNO_3) was added and left to stand at room temperature for 30 min.

After that, the mixtures were heated to the boiling point on a hot plate or sand bath and the temperature was kept close to the boiling point for exactly 5 min (boiled gently). Solutions were left to cool down, then transferred without filtration into volumetric flasks and filled up to 100 mL with de-ionised water. Final solutions were stored in plastic bottles.

Elements to be determined were: As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn, K, Al and Be. (14 elements in total. Some laboratories did not determine all of these elements e.g., in our laboratory beryllium was not analysed.)

RESULTS AND DISCUSSION

At first the results of the Hungarian Geological Survey – Geological Institute of Hungary laboratory are looked at, obtained using our routine open vessel aqua regia leaching as described in the 'Experimental' section of this article.

In Fig. 1 our analysis results of the so-called monitor sample are shown in the individual analytical runs. This monitor sample was included in each sample batch. The obtained concentration values were compared to the median values calculated from all of the results by the ISE. For several elements a leaching efficiency of about 100% was produced, mostly in case of the chacophile elements.

Probably the most striking deviation can be seen in case of sodium. In some periods relatively acceptable leaching efficiency was obtained, while in other runs a significant positive error was produced. This fact can be simply explained by the fact that the

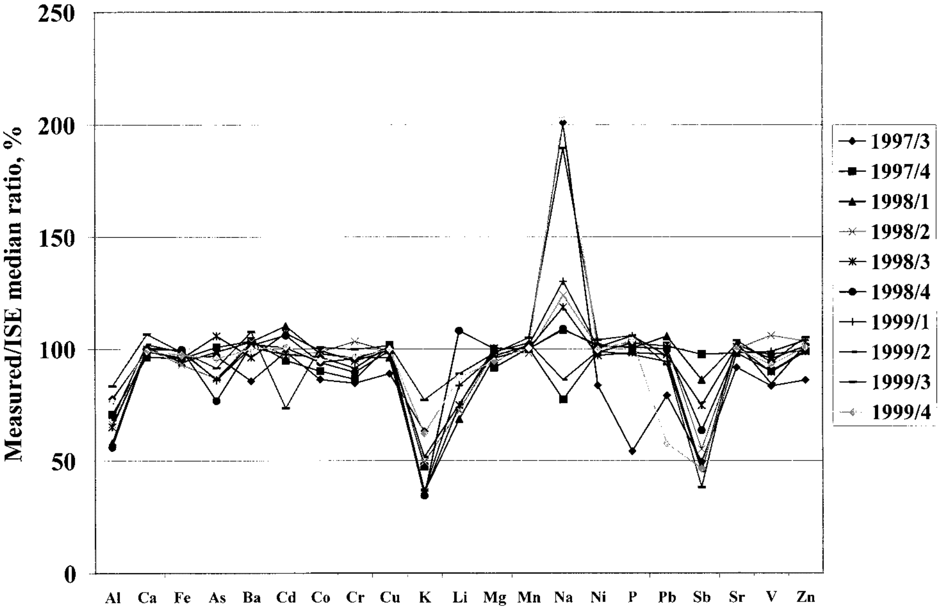

FIGURE 1 Leaching efficiency of individual elements in the monitor sample (in each analytical run) analysed in the laboratory of the Hungarian Geological Survey – Geological Institute of Hungary (as percentage of the ISE median values).

sodium concentration of the sample was very low and sample can easily be polluted by sodium in this concentration range. In the case of antimony mostly a negative error was produced i.e., measured concentration values were often below the ISE median value. Here, analyte loss during the (open vessel) evaporation step was suspected. In an interesting manner, this difference was significantly less in case of arsenic and cadmium.

Analytical results of aluminium and potassium were really problematic. For these elements the concentrations obtained were very low compared not only with the results produced after total decomposition but also with the ISE median (calculated for the ‘‘so-called total’’ element contents).

Of course, inefficiency of our open vessel aqua regia leaching method was suspected.

The majority of the laboratories participating at the ISE scheme use microwave assisted aqua regia digestion of the samples. This leaching method is much more effective than the open vessel digestion procedure.

To check this assumption we carried out the digestion of some selected samples by both techniques and calculated the percentage ratio of the open and closed vessel digestion. All four samples of ISE Period 3 in 1998 were included in this study (four replicates per sample). Ratios of measured concentration values (open vessel system/closed system) were calculated for each element. Average values are listed in Table VI (percentage values). As can be seen, there are several elements showing significant differences between the open vessel aqua regia leaching and closed system decomposition. The most affected elements are titanium, potassium and aluminium.

TABLE VI Comparison of open and closed system digestion methods: percentage ratios of the measured concentrations

Element	*Percentage ratio of the concentrations obtained by different decomposition methods (open/closed system)* (%)
Cr	60–70
Zn	95–100
Ni	95–100
Ba	65–75
Mn	95–100
Mg	85–90
Al	27–56
Cu	95–100
Ti	15–28
Sr	90–95
As	80–100
Mo	100
P	95–100
Pb	95–100
Co	70–80
Cd	95–98
Fe	90
V	50–70
Ca	95
Na	50–98
Li	60–65
K	16–40

The importance of harmonising the digestion step was raised by this study. Decomposition procedures made by different methods were not comparable in this way. Differences occurring because of possible analytical errors cannot be separated from deviations caused by the application of different methods.

For the problematic elements mentioned above, most of the INCO laboratories reported data which were similarly much lower than the ISE median, except for one laboratory. Unfortunately these large differences between replicates masked any differences between laboratories. The only laboratory reporting the highest results for "so-called total" analyses used a closed system decomposition method, whereas all others used an open method. To make the results of participant laboratories more comparable, a new standardised digestion method was designed, called the "Warsaw method". Using this method by each laboratory, results show only the between-laboratory differences, while between-method differences are filtered out.

"Warsaw Experiment"

In view of the discrepancies in values reported by laboratories for the "so-called total" concentration data, it was agreed that the laboratories should carry out the analysis of sample 2 (river clay, monitoring sample) using the same method as far as possible. The main aim of this exercise was to see whether the variation of the data reported so far could be reduced by the adoption of a 'standard' protocol.

This validation experiment was set up to investigate the variations between the participants' data when they all use the same method of sample dissolution. The method was designed to be easy for the laboratories to adopt in the premises and was based on the well-known principles of partial leaching with aqua regia. This experiment was initiated in September 1998 during the meeting in Warsaw (hence its name). Study was designed to investigate the "between laboratory" variations for a specific number of "so-called total" elements.

The "Warsaw method" was not necessarily designed for widespread and routine use for participant laboratories. We only wanted to test the degree of the between-laboratory differences when using a (relatively) standardised method. Five parallel analyses were made from the sample by each laboratory.

It is necessary to mention that the development of the "Warsaw method" did not happen without discussions. The final recipe was accepted but remained controversial. Possible problems were expected as follows: The method could be considered as a "gentle method" i.e., large portion of the original sample would remain insoluble. Moreover, the boiling time might be difficult to keep exactly (prone to subjective factors).

Actually, sceptics were (at least partly) justified by the results.

The analytical results produced in the individual laboratories by the "Warsaw method" were in good agreement for many elements between the laboratories. Results for some chalcophile elements are shown in Table VII. In order to demonstrate it better, not the concentration values but the percentage ratio of the obtained concentration values compared to the ISE median values were calculated. It can be seen, however, that for some volatile elements significant differences were found, possibly because of the subjective factors in starting of the boiling time. A typical example was arsenic.

TABLE VII Leaching efficiency of some selected elements in the monitor sample analysed using the "Warsaw method" by the individual institutes (chalcophile elements)

Lab. code	*Measured/ISE median ratio* (%)				
	As	*Cu*	*Mn*	*Pb*	*Zn*
GAL	102 ± 1.60	98.9 ± 0.92	93.6 ± 1.04	104 ± 1.15	102 ± 0.84
MAFI	91.0 ± 1.50	96.5 ± 1.51	102 ± 1.21	97.8 ± 3.25	97.9 ± 1.26
VICTORY	n.d.	99.9 ± 0.60	n.d.	99.1 ± 1.94	90.7 ± 1.10
TYRKEY	n.d.	105 ± 0.49	104 ± 0.39	115 ± 1.39	94.7 ± 0.43
JMCK	80.5 ± 5.90	100 ± 3.42	100 ± 1.74	106 ± 2.88	97.8 ± 1.80
HSIGLTLABA	n.d.	97.2 ± 0.94	91.4 ± 0.87	94.3 ± 1.61	95.8 ± 2.00
GEOPRA	87.0 ± 3.18	103 ± 0.92	102 ± 0.78	104 ± 2.41	99.7 ± 0.67
ESPOO	119 ± 6.23	77.7 ± 15.2	105 ± 0.99	112 ± 2.03	106 ± 0.57
RGDGEOCHEM	89.1 ± 0.74	105 ± 1.40	88.8 ± 1.00	101 ± 1.68	91.5 ± 0.23
ANALGEO	97.2 ± 2.19	89.1 ± 0.88	95.2 ± 1.06	84.8 ± 1.44	90.8 ± 0.48

n.d. = not determined.

TABLE VIII Leaching efficiency of some selected elements in the monitor sample analysed using the "Warsaw method" by the individual institutes (mostly refractory elements)

Lab. code	*Measured/ISE median ratio* (%)				
	Al	*Be*	*Cr*	*K*	*V*
GAL	52.8 ± 0.60	53.2 ± 1.67	87.6 ± 2.28	33.5 ± 0.61	83.7 ± 3.13
MAFI	46.7 ± 1.43	n.d.	82.7 ± 2.62	26.3 ± 0.99	83.2 ± 2.34
VICTORY	n.d.	n.d.	n.d.	n.d.	n.d.
TYRKEY	n.d.	n.d.	110 ± 2.28	31.3 ± 1.24	n.d.
JMCK	42.8 ± 1.07	63.1 ± 3.44	78.6 ± 1.27	23.2 ± 0.71	71.5 ± 1.13
HSIGLTLABA	n.d.	n.d.	68.9 ± 1.20	74.3 ± 0.76	n.d.
GEOPRA	50.1 ± 0.61	104 ± 6.44	94.0 ± 1.43	31.8 ± 0.18	84.7 ± 7.81
ESPOO	39.5 ± 0.17	71.4 ± 0.58	82.9 ± 0.68	21.1 ± 1.00	79.0 ± 0.96
RGDGEOCHEM	n.d.	69.7 ± 0.89	74.4 ± 0.07	n.d.	n.d.
ANALGEO	62.5 ± 1.28	77.1 ± 1.48	80.4 ± 1.48	48.4 ± 1.77	83.4 ± 1.12

n.d. = not determined.

Differences in dissolution efficiency of the elements which are able to build into the silicate lattice (e.g., aluminium, potassium) or are present in refractory mineral grains (e.g., chromium) are more significant than for the elements mentioned above. This fact could be attributed to the "gentle" experimental conditions. The too short boiling time has relatively stronger effect on the refractory elements comparing to the chalcophile ones. Some typical examples such as Cr, V, Be, Al and K are shown in Table VIII.

Apparently the "Warsaw method" still needs some adjustment to achieve a higher degree of uniform results.

A reason for the ISE median being higher than most of the "Warsaw experiment" results was thought to be because the majority of the ISE laboratories used a closed digestion, whereas open vessels were used for the "Warsaw experiment". This would explain why elements such as Al, Be, Cr and K were much lower in the "Warsaw experiment", in which the digestion conditions were less aggressive than those usually employed by the INCO laboratories.

In Figs. 2 and 3 a comparison of the main types of the leaching methods is shown. Typical methods are represented here by results obtained in the respective laboratory (marked by ISE laboratory code).

MAFI (Hungarian Geological Survey – Geological Institute of Hungary) employed open vessel leaching by concentrated aqua regia, including an evaporation step. Using this method, losses of volatile elements may occur especially as control of the evaporation step might be difficult. If this step is prolonged for some reason, undesirable problems mentioned above can arise.

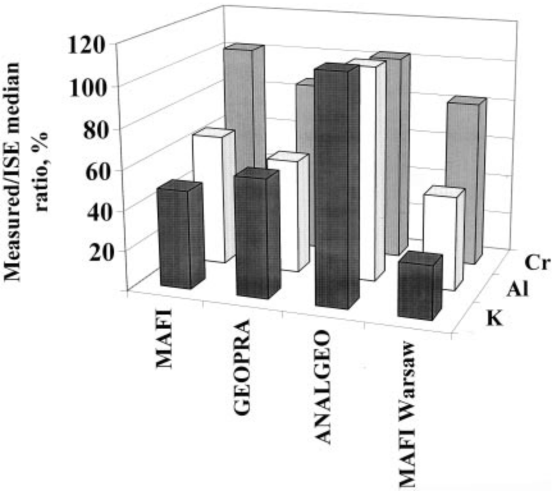

FIGURE 2 Comparison of leaching efficiency of some selected elements in the monitor sample analysed using different methods (mostly refractory elements): Laboratories marked by their laboratory code used their own leaching methods; Laboratory marked by MAFI Warsaw means the laboratory of the Geological Survey of Hungary, using the consensus "Warsaw" method.

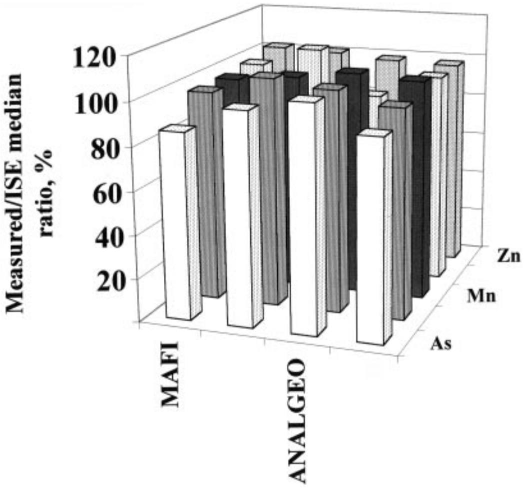

FIGURE 3 Comparison of leaching efficiency of some selected elements in the monitor sample analysed using different methods (chalcophile elements): Laboratories marked by their laboratory code used their own leaching methods; Laboratory marked by MAFI Warsaw means the laboratory of the Geological Survey of Hungary, using the consensus "Warsaw" method.

GEOPRA applied leaching by diluted aqua regia, using boiling under reflux. This method is "gentle", so acidic attack cannot be considered aggressive enough to dissolve some elements. As an advantage, losses of volatile elements are eliminated.

ANALGEO performed leaching by concentrated aqua regia, using a microwave digestion unit. This method is much better controllable as other methods above. Of course, losses of volatile elements are completely eliminated.

Resuls obtained by leaching using the standardised common ("Warsaw") method are presented on the example of Hungarian Geological Survey – Geological Institute of Hungary (MAFI). This method is fairly "gentle", for some elements it is not aggressive enough. Reproducibility can be predicted to be questionable: to catch the exact starting time of boiling is prone to subjective factors, so the actual length of the boiling period might be different. This fact might influence the efficiency of the acidic attack. Being an open vessel method, losses of volatile elements might occur.

In Fig. 2, examples for elements such as chromium, aluminium and potassium are shown. It can be seen that also the uniform "Warsaw" method, being an open vessel system, lagged behind in efficiency the microwave assisted digestion. In this case, the further factors like the use of an evaporation step or boiling under reflux (as it was included into MAFI and GEOPRA methods), did not increase the digestion efficiency significantly. The role of these factors, however, could be important as it can be seen on the example of potassium. In this case, the efficiency of the "Warsaw method" was by far the poorest.

The behaviour of the volatile arsenic was very interesting and met the expectations. (Fig. 3) It could clearly be seen that losses can occur during open vessel leaching especially if applying also an evaporation step (MAFI method). Boiling under reflux could improve the leaching efficiency (GEOPRA method). The most accurate results were produced after microwave assisted digestion, of course (ANALGEO method). In the case of other investigated chalcophile elements (Zn, Cu, Mn) satisfactory results were obtained using any of digestion method.

CONCLUSIONS

To sum up our experiences, we can draw the following conclusion.

The results of the "Warsaw" method indicate that statistically significant variations can be experienced if the results originate from different laboratories even using the same leaching method. If our aim is the determination of the so-called mobile or leachable element contents of samples, we have to define our leaching methods much more exactly. Comparable results for the partial leaches can be obtained only in the case when the sample digestion is better controlled (e.g., microwave techniques with controlled temperature and pressure in closed digestion vessels, together with detailed instrumental protocols).

The INCO-Copernicus project clearly revealed that the between-laboratory effects are significant for the "so-called total" concentrations because almost all of the participants used open vessel leaching technique. In international mapping programmes and in data collection for the calculation of baseline levels, the samples produced for these purposes should be analysed by well-defined methods only and the analyses should be extremely strictly controlled both by using CRMs (Certified Reference Materials) and a suitable quality control (QC) system.

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