

ANALYTICAL BACKGROUND OF CARLIN-TYPE GOLD PROSPECTION IN HUNGARY

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ABSTRACT

Analytical methods used for the purposes of the project J.F. No. 435 "Potential for Carlin-type gold deposit in Hungary" are described in this paper. Ag, As, Au, Sb and Tl were determined from the samples after aqua regia decomposition and Hg directly from the solid sample (by AMA 254 instrument, dedicated to mercury determination). Determination of gold was performed by electrothermal (graphite furnace) atomization atomic absorption spectrometry (GF-AAS), after separation and preconcentration by extraction with isobutylmethylketon. Other elements were determined by inductively coupled plasma mass spectrometry (ICP-MS). Results of the ongoing "Geochemical mapping project" at the Geological Institute of Hungary including the stream sediment survey of the hilly areas in Hungary were also involved into interpretation of the Carlin gold project. In this project, a considerably wider range of elements (18 elements) was determined. In this case, determination of mercury and gold was carried out in the same way as it was done during the Carlin gold project. Determination of arsenic and antimony was performed by hydride generation atomic absorption spectrometry (HG-AAS) and silver was analyzed by flame atomization atomic absorption spectrometry (Flame-AAS). Further elements were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Analytical methods used were checked by comparison with different analytical methods. Results show pretty good agreement.

1. INTRODUCTION

Chemical analysis of the samples collected in the frameworks of the Carlin gold project was performed in the laboratory of the Geological Institute of Hungary. Analytical background of the research can be summarized as follows.

Determination of the aqua regia leachable elements was carried out. Elements to be determined were going into solution probably in 100 per cent or close to this ratio, because of their chemical characteristics.

Chemical analyses were carried out for the elements as Au, Ag, As, Sb, Hg and Tl.

Determination of gold and mercury was done by atomic absorption spectrometry and the other elements were determined by inductively coupled plasma mass spectrometry technique.

We used this analytical scheme because: it was an important point of view of convenience to use multi-elemental method if possible. That is why the use of ICP-MS is practical (JARVIS et al. 1992, HALL 1992, BRENNER and ZANDER 1996). For the gold and mercury, however, despite of their high atomic mass and freedom from spectral interferences, we could not obtain proper sensitivity by ICP-MS technique.

Gold will be ionized only in 51% in the plasma. Despite of that, the limit of detection seems favorable, it can be calculated to be about 10-20 ppb. This value, however, is much higher than the average abundance of gold (which is about 2 ppb). That is why we had to choose the atomic absorption method with preconcentration and separation. The latter method does not have any competitor in this field.

For the mercury, it was not the case. In fact, mercury will be ionized only in 38% in the plasma. Detection limits are still sufficient to fulfil the requirements of this research. Mercury, however, produces very strong memory effect. Aspirating mercury solution into the plasma, the wash-up time is very long even at very low concentra-

tions (e.g. using 10 µg/l solution). So, we could not obtain reliable results after aspirating a calibration solution or a sample solution with higher mercury concentration. That is why determination of mercury by ICP-MS is generally avoided. Fortunately, a very simple and reliable analytical method i.e. cold vapour atomic absorption spectrometry (directly from solids) is available (BARTHA et al. 1996).

Results of the stream sediment survey were also utilized. During this project, a wide range of elements was determined from the samples, namely: Ag, As, Au, Ba, Cd, Co, Cr, Cu, Hg, K, Li, Mn, Mo, Ni, Pb, Sb, Sr and Zn. Determinations were performed mostly by inductively coupled optical emission spectrometry (ICP-OES), utilizing multi-elemental characteristic of the method (JARVIS and JARVIS 1992, BRENNER and ZANDER 1996). Detection limits were generally low enough to fulfil the requirements of the survey but for some elements, atomic absorption spectrometry (AAS) was applied, using different atomization methods: electrothermal (graphite furnace) atomization (for gold, after preconcentration by MIBK extraction), hydride generation (for arsenic and antimony), cold vapour technique (for mercury) and flame atomization (for silver). Interpreting results for the purposes of Carlin research, only analysis results for Ag, As, Au, Ba, Hg and Sb were utilized (KORPÁS et al. 1999).

2. INSTRUMENTATION

In the laboratory of the Geological Institute of Hungary a considerable technical infrastructure is available.

ICP-MS measurements were performed on a commercial quadrupole system (VGE PlasmaQuad II STE, VG Elemental, Winsford, Cheshire, UK). Ion optics was optimized for indium, a medium-mass element.

Determination of gold was performed by a SpectrAA-10BQ atomic absorption spectrometer (Varian, Melbourne, Victoria, Australia), equipped with a Varian GTA-95 Graphite Furnace Unit. Sample introduction was done automatically, using a PSD Programmable Sample Dispenser. A commercial Varian uncoded hollow cathode lamp and the 242.8 nm resonance line was used. Background correction was made by deuterium lamp method. Partitioned coated graphite tubes were used (Varian Part. No.: 63-100012-00).

Mercury was determined by cold vapour atomic absorption spectrometry, directly from the solid sample. AMA 254 instrument (Advanced Mercury Analyzer) was used (made by Altech, Czech Republic, distributed by LECO). Sample was placed into sampling boat and introduced into a decomposition tube. Sample was there first dried and then thermally decomposed (or even burned) in oxygen flow, by controlled heating of the decomposition furnace. Oxidation was finalized in a catalytic furnace and some of combustion products were trapped here. Mercury vapours were selectively trapped by a gold-containing amalgamator. In a second stage, mercury was released by heating of amalgamator and transferred into the measuring cells where measurement of absorbance was carried out. In case of low mercury concentrations, determinations were carried out directly from the solid sample. Samples containing higher concentrations of mercury were decomposed and solution was analyzed.

ICP-OES determinations were performed by a combined instrument (sequential instrument also equipped with a 20-channel polychromator) (JY70, Jobin Yvon, Longjumeau, France).

During the stream sediment survey, several elements were determined by atomic absorption spectrometry, using different atomization methods. Instrument used was a SpectrAA-10BQ atomic absorption spectrometer (Varian, Melbourne, Victoria, Australia). For flame atomization, a commercial 10 cm burner head (Mark VI) was used. For the determination of hydride forming elements, instrument was equipped with a continuous hydride generation unit, made by Labtech (Brno, Czech Republic). Determination of gold and mercury was performed as written above.

3. CHEMICALS AND REAGENTS

Distilled water (glass distillation unit, made by SIMAX, former Czechoslovakia) was used throughout the work. In ICP-MS work (for dilution of samples and preparation of calibration standards), ultrapure water, with a resistivity of 18 MΩcm, was used, obtained from a Purite HP Still Plus system (Purite Ltd., Thame, Oxfordshire, UK). Hydrochloric acid 36% and nitric acid 70% used for decomposition were BDH (Poole, Dorset, UK) products, "Spectrosol" quality. For preparation of ICP-MS calibration standards, nitric acid 65% of "Suprapur" quality (Merck, Darmstadt, Germany) was used. "Procedure blank" was prepared by each batch of samples.

Stock solutions for ICP-MS calibration standards were mono-elemental solutions (1 g/l each) and were from BDH, "Spectrosol" grade (Ag, As and Sb) and from SPEX Industries, Inc. (Edison, NJ, USA) (TI, SPEX Plasma Standard solution, PLTL2-2Y). These solutions were diluted to give concentration of 10 mg/l. Calibration standard solutions were made up by mixing and dilution of these latter solutions. Final acid concentration was 1% of

nitric acid. (Nitric acid 65% used throughout ICP-MS work was Merck product, "Suprapur" quality). Stock solution for indium internal standard was a mono-elemental solution (1 g/l) and was from BDH, "SpectrosoL" grade. This solution was diluted to give a concentration of 1 mg/l. The latter solution was added to the sample solutions to give a final In concentration of 10 µg/l.

Gold stock solution for GF-AAS calibration standards was mono-elemental solution (1 g/l) and was from BDH, "SpectrosoL" grade. Calibration standard solutions were made up by stepwise dilution of this stock solution. Final acid concentration was about 1.2 mol/l of hydrochloric acid. Isobutylmethylketone used for gold extraction was from BDH, "AnalaR" grade.

4. ANALYTICAL METHODS

4.1. Sample decomposition methods

Decomposition is a key question in course of the chemical analysis. In geological and geochemical research it is especially difficult to decide which decomposition method would be the most suitable one for the task in question. Using methods providing "complete" decomposition, several problems will be faced (increased total dissolved solids content, use of hydrofluoric acid etc.). Analyzing chalcophile elements, however, some of these problems can be diminished. In this case, dissolution of the samples by some acidic mixture (mostly aqua regia) is completely sufficient (CHAO and SANZOLONE 1992, TOTLAND et al. 1992, BERTALAN et al. 1999)

Two different dissolution techniques were applied. One of them is decomposition in closed, high-pressure bomb which allows also the volatile mercury to be determined. (PTFE bomb vessels in stainless steel housing by Parr Instruments, Moline, Illinois, USA, were used.) Another decomposition is open vessel dissolution by aqua regia which is suitable to handle also large sample portions.

For the open vessel decomposition, it was advisable to roast the samples previously. Roasting was necessary because of the weak solubility of the possible arsenopyrite content of the sample. Roasting was performed in electric furnace, held the sample at 700 °C for 2 hours. Relatively weakly soluble sulfides were oxidized during roasting. Sample weight was 5 g. After finishing roasting, samples were transferred into glass beakers, 12.5 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid were added and samples were evaporated to dryness on waterbath. Residues were dissolved by 10 ml of 1:1 diluted hydrochloric acid and solutions were made up to 50 ml. Final sample concentration was 100 g/l. Determination of gold was carried out from an aliquot of this solution by graphite furnace atomic absorption spectrometry (GF-AAS) after preconcentration and separation by organic extraction. Determination of arsenic, antimony, silver and thallium was performed by ICP-MS technique after proper dilution of sample solution. ICP-OES and AAS determinations were performed from this solution as well, also after proper dilution of sample solution.

Performing high pressure decomposition, 0.5 g of sample was weighed into PTFE vessel of the bomb. Weighed samples were suspended with some drops of distilled water, 2 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid were added, bombs were closed and held at 150 °C for 1 hour in drying oven. After cooling down, sample solutions were made up to 100 ml. Sample concentration was 5 g/l. These solutions served for the determination of higher mercury concentrations (much higher than 10 ppm) by cold vapour technique atomic absorption spectrometry. In this case, determination of mercury could not be carried out directly from the solid sample because mercury vapours could be condensed in the catalytic furnace of the instrument and could not be removed from there any more.

Determination of mercury (below 10 ppm) was made directly from solid sample.

4.2. ICP-MS determinations

Elements as As, Ag, Sb, Tl were determined by ICP-MS method. Analyses were performed by a VG Plasma-Quad II STE ICP-MS instrument. Sample solution of 100 g/l sample concentration was diluted 100-fold, obtaining solution of 1 g/l sample concentration to measure. 10 µg/l In was added as internal standard into this solution. Detection limit of the measurements was 0.2 ppm for arsenic and 0.02 ppm for the other elements. Instrument operating parameters are listed in Table 1.

In the ICP-MS determinations, only arsenic could be considered as critical element as it can be subjected to spectral interferences. Arsenic has got only one natural isotope ⁷⁵As and a polyatomic ion, with a mass number of 75, formed from argon and chlorine atoms, will cause an overlap, a spectral interference. In our case the system contained chloride ions because during the open vessel decomposition, evaporation residue was dissolved by hy-

ICP-MS operating parameters

Table 1

Instrument	VG Elemental PlasmaQuad II STE
Plasma	all argon
Forward power	1350 W
Reflected power	<5 W
Coolant gas flow	13.5 l/min
Auxiliary gas flow	1.4 l/min
Nebuliser gas flow	0.928 l/min
Peristaltic pump	Gilson Minipuls 3
Uptake rate	about 1 ml/min
Nebuliser	V-groove
Spray chamber	double-pass, water-cooled (10 °C)
Sampling cone type	Ni, 1 mm orifice
Skimmer	Ni, VG design
Acquisition mode	scan
Detector mode	PC
Channel/amu	20
Dwell time	320 μ s
Acquisition time	60 s
Scanned regions	71.6 - 79.4 amu
	103.6 - 125.4 amu
	199.6 - 206.4 amu
Internal standard	^{115}In (10 $\mu\text{g/l}$)

drochloric acid. For the ICP-MS determination, however, this solution was diluted 100-fold, so the final concentration of hydrochloric acid was about 0.01 mol/l. According to our experiences, this concentration did not cause serious problem and could be corrected properly by mathematical methods, using peak with mass number of 77. It was proven by comparison with another independent analytical methods (see Section 5). Results obtained by hydride generation AAS or ICP-OES showed very good agreement with the ICP-MS results.

4.3. Analysis of gold

Gold content of samples was determined from the solution obtained by open vessel decomposition (final sample concentration of 100 g/l), after preconcentration by isobutylmethylketon, by electrothermal (graphite furnace) atomization atomic absorption spectrometry (GF-AAS). Analyses were performed by a Varian SpectrAA-10BQ instrument. Graphite furnace operating parameters are listed in Table 2.

10 ml of sample solution was extracted by 2 ml of isobutylmethylketon for 2 minutes and the phases left to be separated. Aliquots of the organic phases were transferred into the autosampler vials. 10 μl of the organic phase was injected into the graphite furnace and analyzed. In case of high gold concentrations, sample solution was diluted by a proper dilution factor and extracted again. Detection limit of the method was 2 ppb Au.

4.4. Analysis of mercury

Mercury was determined by cold vapour atomic absorption spectrometry (CV-AAS). AMA 254 instrument was used. In case of low mercury concentrations, determinations were carried out directly from the solid sample. Sample weight was 100 mg. Instrument operating parameters are listed in Table 3. Detection limit was 0.1 ppb Hg.

Graphite furnace operating parameters*Table 2*

Step No.	Temperature (°C)	Time (s)	Gas flow (l/min)	Gas type	Read command
1.	95	5.0	3.0	Normal	No
2.	120	5.0	3.0	Normal	No
3.	150	10.0	3.0	Normal	No
4.	300	5.0	3.0	Normal	No
5.	700	30.0	3.0	Normal	No
6.	1000	2.0	0.0	Normal	No
7.	2600	1.0	0.0	Normal	Yes
8.	2600	2.0	0.0	Normal	Yes
9.	2600	2.0	3.0	Normal	No

Mercury analyzer operating parameters*Table 3*

Stage	Temperature (°C)	Time (s)
Drying	120	60
Pyrolysis	850	150
Waiting	120	40
Measurement	Release: 950 Reading: 120	45

Operating parameters of the ICP-OES instrument*Table 4*

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)
Integration time	0.5 s (poly) to 5 s (mono)

Integration time depends on using polychromator or monochromator and depends on the element in question (relative intensity of the selected line, wavelength, quality of background etc.).

Samples containing higher concentrations of mercury were decomposed and solution was analyzed. 100 µl of sample solution was measured onto an amount of ignited sample. This served to avoid splashing of sample and damage of sample boat by the acidic solution. After this, analysis cycle was started. Detection limit was 20 ppb Hg, calculated for solid sample.

Element	Wavelength (nm)	Background (nm)	Calibration concentration (mg/l)	Calibration conc. in rock (ppm)	Det. lim. in rock (3 σ) (ppm)
Cr	205.552 p	+0.0635	1.0	200	2
Zn	213.856 p	+0.0635	1.0	200	1
Co	228.616 p	-0.0635	1.0	200	2
Ni	231.604 p	+0.0635	1.0	200	2
Ba	233.527 p	+0.0635	1.0	200	0.5
Cu	324.754 p	-0.0635	1.0	200	0.5
Sr	407.771 p	+0.0635	1.0	200	1
Mn	257.610 p	+0.1143	1.0	200	0.2
Mo	202.030 m	-0.0295	1.0	200	1
Pb	220.353 m	+0.0206 -0.0235	1.0	200	5
Cd	228.802 m	+0.0586	1.0	200	1
Li	670.784 m	-0.0595	1.0	200	0.5
K	769.896 m	-0.0447	100	2.408% (K ₂ O)	20

m=using monochromator
p=using polychromator

Wavelengths used in atomic absorption spectrometry and detection limits obtained

Table 6

Element	Wavelength (nm)	Det. lim. in rock (ppm)
As	197.26	0.5
Sb	206.83	0.5

4.5. ICP-OES determinations

Analyses were performed by a Jobin Yvon JY70 instrument. Sample solution of 100 g/l sample concentration was diluted 20-fold, obtaining solution of 5 g/l sample concentration to measure. Internal standard was not used. Instrument operating parameters are listed in Table 4.

Spectral lines chosen for the determinations and detection limits are listed in Table 5.

4.6. Analysis of arsenic and antimony

Arsenic and antimony content of samples was determined by hydride generation AAS. Varian SpectrAA-10BQ instrument equipped with a hydride generation unit (Labtech, Brno, Czech Republic) was used. Sample solution of 100 g/l sample concentration was diluted 10-fold, obtaining solution of 10 g/l sample concentration to measure. To bring the analytes into proper valence state, pre-reduction of the sample was carried out by potassium iodide. Spectral lines chosen for the determinations and detection limits are listed in Table 6.

4.7. Analysis of silver

Silver content of samples was determined by flame atomization AAS. Varian SpectrAA-10BQ instrument was used. Sample solution of 100 g/l sample concentration was diluted 2-fold, obtaining solution of 50 g/l sample concentration to measure. Wavelength used was 328.10 nm. Detection limit (3 σ) is 0.3 ppm, calculated for the original rock sample.

5. COMPARISONS WITH DIFFERENT ANALYTICAL METHODS

Analytical methods used in the course of the project were checked for some elements by analyzing a number of samples by independent analytical methods and by comparison of results. During this study, results obtained by inductively coupled plasma mass spectrometry (ICP-MS) were compared with data produced by electrothermal (graphite furnace) atomization atomic absorption spectrometry (GF-AAS, in case of silver), flame atomization atomic absorption spectrometry (Flame-AAS, also for silver), hydride generation atomic absorption spectrometry (HG-AAS, in case of arsenic and antimony) and inductively coupled plasma optical emission spectrometry (ICP-OES, also for arsenic).

Firstly, comparison of silver results is shown as follows (Figs. 1, 2 and 3). More than 50 selected samples were analyzed both by inductively coupled plasma mass spectrometry (ICP-MS) and by electrothermal (graphite furnace) atomization atomic absorption spectrometry. Analytical results are plotted (Fig 1). Plain line is the ideal case: if results were identical. Lower concentration values are shown in a separate graph (Fig. 2).

Agreement is rather good or at least acceptable.

Flame atomization atomic absorption spectrometry is suitable to measure also higher concentration values. Fig. 3. shows comparison of analytical results of about 80 samples, obtained by ICP-MS and Flame-AAS methods.

Agreement is pretty good except for the higher concentration values where some deviation can be seen – ICP-MS values are a bit higher. It is very common in the ICP-MS technique to get some positive error analyzing much higher concentrations than the highest calibration solution. In this case, proper dilution of the sample solutions can completely eliminate this source of error.

As it was mentioned above (Section 4.2.), ICP-MS determination of arsenic is prone to chloride interferences. This problem, however, can be eliminated using mathematical corrections. To check the applicability of these correction methods and the correctness of the ICP-MS analyses, about 150 selected samples were analyzed both by inductively coupled plasma mass spectrometry (ICP-MS) and by inductively coupled plasma optical emission spectrometry (ICP-OES). For the comparison, results were plotted (Fig. 4).

Results show pretty good agreement. Lower concentration values are plotted also in separate graphs (Figs. 5 and 6).

It can be seen very well, that the agreement between the results is extremely good even for the low concentrations. This agreement is also a good proof of the fact that none of these analytical methods are influenced by the possible interference sources (chloride interference in ICP-MS and interference by iron in ICP-OES).

ICP-MS analysis results were also checked by analyzing some selected samples by hydride generation atomic absorption spectrometry (HG-AAS). In the latter, also a separation of the analyte from the matrix is done, so possible interference effects will be significantly diminished. Plot of the results is shown in Fig. 7.

Results are in very good agreement also in this case.

HG-AAS analysis of antimony from some selected samples was also carried out. Plot of the results is shown in Fig. 8.

Results show good agreement again.

Determination of mercury was also involved in this study. Analysis results for mercury, obtained by cold vapour atomic absorption spectrometry (CV-AAS) directly from the solids and from a solution of decomposed sample, respectively, were also compared. Plot of results of about 100 samples is shown in Fig. 9.

Agreement is good. That means, occurrence of the mercury in the sample is rather homogeneous, so small sample weight used in the direct solids analysis will not cause significant problem.

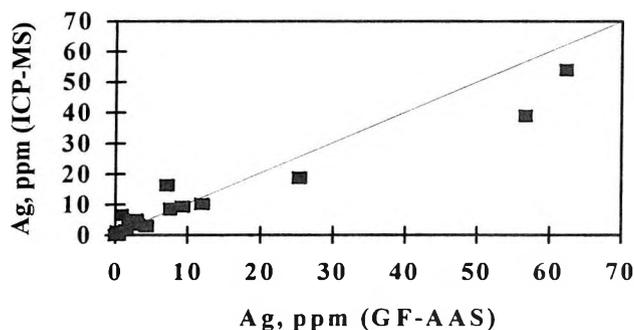


Fig. 1: Determination of silver from rock samples: comparison of ICP-MS and GF-AAS methods

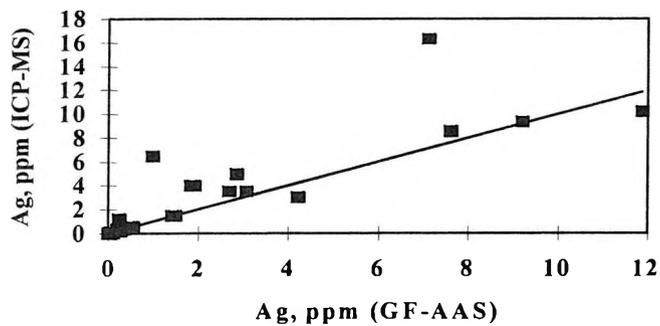


Fig. 2: Determination of silver from rock samples: comparison of ICP-MS and GF-AAS methods (lower concentration values only)

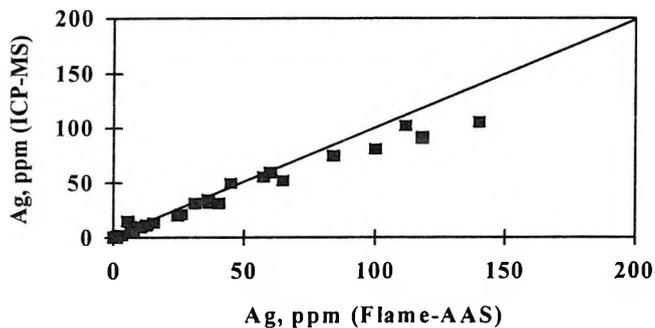


Fig. 3: Determination of silver from rock samples: comparison of ICP-MS and Flame-AAS methods

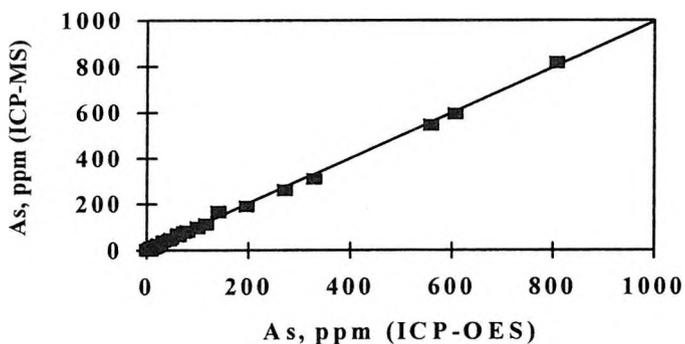


Fig. 4: Determination of arsenic from rock samples: comparison of ICP-MS and ICP-OES methods

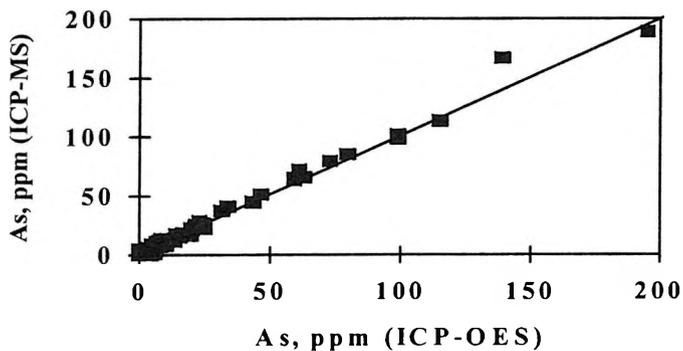


Fig. 5: Determination of arsenic from rock samples: comparison of ICP-MS and ICP-OES methods (lower concentration values only)

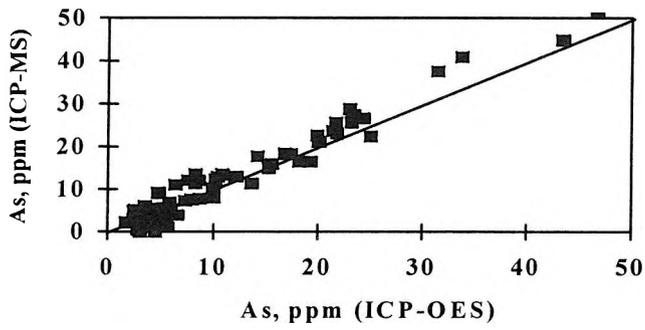


Fig. 6: Determination of arsenic from rock samples: comparison of ICP-MS and ICP-OES methods (concentration values below 50 ppm only)

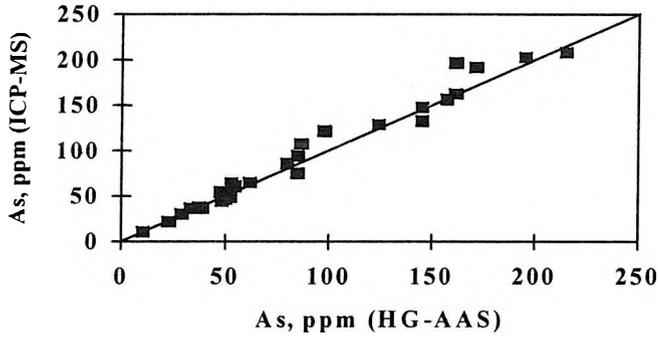


Fig. 7: Determination of arsenic from rock samples: comparison of ICP-MS and HG-AAS methods

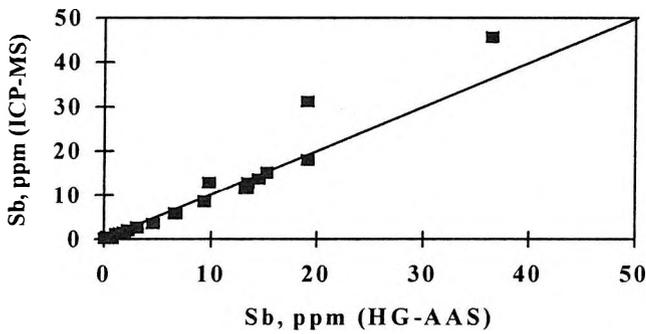


Fig. 8: Determination of antimony from rock samples: comparison of ICP-MS and HG-AAS methods

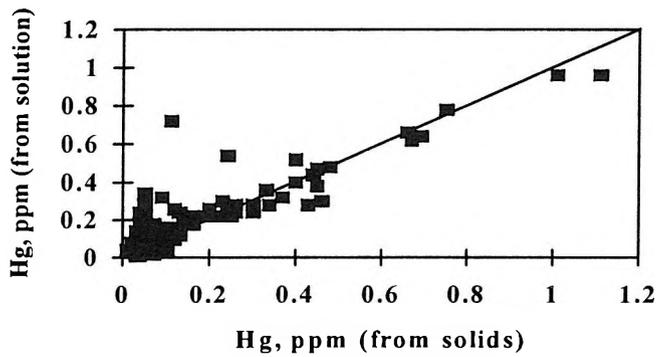


Fig. 9: AAS determination of mercury from rock samples: comparison of analysis directly from the solids and analysis from solutions of decomposed samples

6. CONCLUSION

Analytical methods used in the course of the Carlin gold project are suitable to solve emerging analytical tasks. Comparison of results with results of different independent analytical methods shows good agreement.

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