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Determination of Gold, Silver and Platinum-Group Elements in Geochemical Reference Materials by Direct Atomic Emission Spectral Analysis Using a Multichannel Analyser Recording Device

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A procedure for the analysis of geochemical samples has been developed based on direct atomic-emission spectrometry for the determination of silver, gold and the platinum-group elements. Instrumentation comprised a DC arc emission two-jet plasmatron coupled to a diffraction spectrograph and multichannel analyser for recording emission spectra. Spectrum analysis used a comprehensive library of spectral lines for practically all elements excited using this emission source. The software programme for the automatic registration of spectra and subsequent data processing are described and results presented for a number of geochemical reference materials.

Keywords: atomic emission spectroscopy, platinum-group elements, gold, silver, reference materials, multichannel analyser, emission spectra.

Une procédure analytique pour la détermination de l'argent, de l'or et des éléments du groupe du platine dans des échantillons géochimiques a été développée par spectrométrie d'émission atomique directe. L'instrumentation comprenait un générateur à plasma (plasmatron-2 jets) par émission en arc continu couplé à un spectrographe de diffraction et à un analyseur multi-canal pour l'enregistrement des spectres d'émission. Un guide de raies spectrales exhaustif a été utilisé pour l'analyse spectrale de l'ensemble des éléments excités par cette source d'émission. Le programme informatique de l'enregistrement automatique des spectres et le traitement ultérieur des données sont décrits et des résultats sont présentés pour de nombreux matériaux géochimiques de référence.

Mots-clés : spectroscopie d'émission atomique, éléments du groupe du platine, or, argent, matériaux de référence, analyseur multi-canal, spectres d'émission.

A number of procedures have been published describing the determination of the platinum-group elements (PGE's: Ru, Rh, Pd, Pt, Os, Ir) and Au in rocks and minerals by inductively coupled plasma-mass spectrometry, but almost all of these involve the preparation and analysis of sample solutions (Date *et al.* 1987, Grégoire 1988, Potts 1998, Totland *et al.* 1992, 1993, 1995, Plessen and Erzinger 1998, Li *et al.* 1998, Amossé 1998). Devices which allow the determination of these elements directly in the solid state deserve particular attention (Yudelevich *et al.* 1984, Cherevko *et al.* 1988, Zolotovitskaya *et al.* 1997). The precision and sensitivity of atomic emission spectroscopy depends on a number of factors, including the choice of excitation source, the method of sample preparation and of sample introduction into the plasma, as well as the instrumentation used for recording optical emission information (Yudelevich *et al.* 1974, Zayakina *et al.* 1991a, b, 1994). In the present work, the results of an investigation into the possibility of using an automatically controlled device for the determination of a large number of elements, among them, gold, silver and the platinum-group elements, in different geochemical reference materials are presented, based on preliminary reports in the Russian literature (Zayakina and Anoshin 1999, Zayakina *et al.* 1999). Much of the software

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currently developed for atomic-emission spectral analysis is oriented to the inductively coupled plasma (Tromp *et al.* 2000) and many such investigations are based on mass spectrometry (Shuttleworth and Kremser 2000). Hence, it is appropriate to describe the procedures used here, including the choice of analytical parameters for the calculation of calibration curves and comparison of results from emission lines selected on the basis of the work of Vasilyeva and Shabanova (1998) for DC arc emission. Special attention in the present work is given to automating the process of recording an analytical signal and the statistical treatment of these signals and the resultant data.

Instrumentation

The instrumentation, shown schematically in Figure 1a, comprises an arc two-jet plasmatron and a model DFS-458 diffraction spectrograph having average dispersion, but high optical efficiency and acceptable resolution. Spectra were recorded using a multichannel analyser (model MAES-10), which incorporated the analogue to digital conversion of emission spectra making them compatible for subsequent data processing.

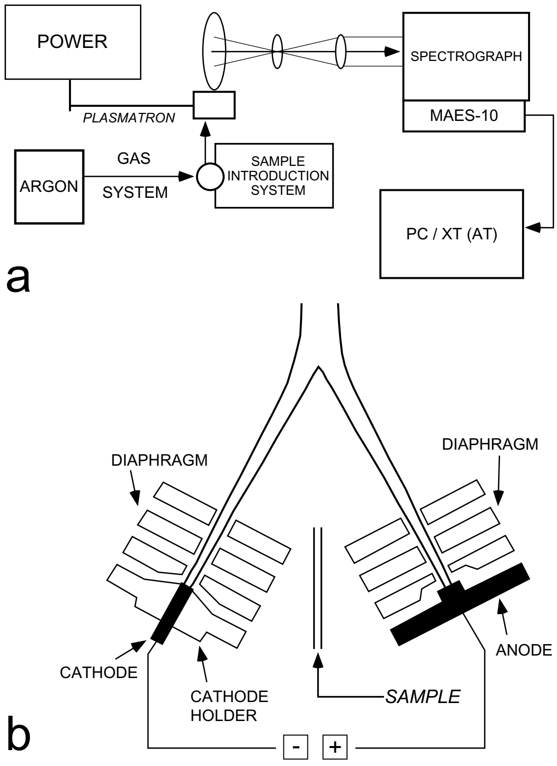

Figure 1. Schematic diagrams of (a) the experimental instrumentation and (b) the plasmatron.

Plasmatron

The arc two-jet plasmatron (Zheenbaev and Engelsht 1983) shown schematically in Figure 1b consisted of anode and cathode assemblies at an angle of 120° to each other. Each assembly had an electrode and three water cooled copper discs separated from each other by rubber rings, so forming a nozzle. The cylindrical cathode was made of thoriated tungsten and was designed with a long consumable portion which was screwed into the copper holder. The anode was made of copper. Argon, the electrode sheathing gas, passed between the electrodes and first copper disc. The gas mixture supporting the plasma (air, argon, hydrogen, etc.) passed between the other discs. A standard rectifier was used as the power supply for the plasmatrons. To initiate arcing between the two electrodes, a special start-up device was used, based on the principle of progressively elongating the arc along the cascade copper discs. The merging of the two plasma jets above the electrodes produced a plasma propagated at a velocity of 20 ms^{-1}.

Sample introduction

The sample was injected between the two plasma jets as shown in Figure 1b as a powder suspended in a gas stream under pressure. A special device was used to disperse sample powders into the gas stream using a pneumatic mechanism. The sample prepared for analysis was placed in an organic glass beaker (10 mm in diameter, 30 mm in depth) and injected into the flow between the plasma streams through a 2 mm diameter tube.

Reference materials and other geological samples were prepared by grinding the sample to a very fine powder, having a particle size of about 5-10 μm. The finely dispersed powder was mixed with graphite powder in a 1:1 ratio. This procedure eliminated any heterogeneity effects that might have been caused when the sample powder was introduced into the plasma.

The operating conditions selected for the simultaneous determination of a large number of elements including gold, silver and the platinum-group elements are shown in Table 1.

Spectrum recording conditions

Emission spectra were recorded and digitised in a format suitable for computer data processing using a

Table 1.
Instrument operating conditions

Voltage of arc	100 V
Current of arc	90 A
Argon consumption:	
for plasma generation	53 ml s^{-1}
for powder injection	15-20 ml s^{-1}
Mass of sample for recording a single spectrum	100 mg
Recording time	6 s
Number of simultaneous elemental determinations	15-20

MAES-10 multichannel analyser system. The size of the MAES-10 diode allowed spectra to be recorded with a dispersion of 0.5 nm mm^{-1} when coupled to a model DFS-458 diffraction spectrograph. The present investigation was undertaken in the wavelength range from 220 to 350 nm using a grating of 1800 grooves mm^{-1} giving a calculated dispersion of 0.48 nm mm^{-1}. The optical system was fitted with a single F = 76 lens and slits designed to view a 2 mm high region of the plasma at a distance of 4-6 mm from the merging plasma.

The application package (Zayakina *et al.* 1999) used for the analysis of atomic emission spectra was developed by the scientific group, Optoelectronika, at the Institute of Automatic and Electrometry of Siberian Branch of Russian Academy of Sciences (SB RAS), Novosibirsk, and comprised the following subprogrammes: A module for the registration of spectral information; a data base comprising the recorded spectra; a module for wavelength calibration; a library of spectral lines of elements; a module for constructing calibration curves, programmes for calculating both the concentration of determined elements; and associated statistical data. The operator could select as an analytical signal the following parameters: intensities of analytical lines (I_l) and the corresponding background (I_b), or their ratio I_l / I_b. Alternatively, the area delimited by the contour of an individual spectral line could be calculated. There is also an option of ratioing intensity data to that of a reference element (I_{ref}), in which case, intensity data are recorded as (I_l / I_{ref}).

The information obtained was recorded on a display in the form of statistically processed values of analytical lines and background intensities or values of concentrations with relevant regression equations and curves. Data obtained using reference samples, the procedure used to record and analyse measurements, and other current analytical information were recorded in the computer and could be used for the subsequent assessment of results.

Certified reference materials

Certified reference materials were prepared for analysis using standard sample preparation procedures detailed in GSO catalogue No 4519-89-4523-89. Two main series of Russian reference samples were used. The first series (SOG-13 and SOG-21) was prepared and certified by the Russian Arbitrage Laboratory at Ural State University (RAL USU) and the second by the Vinogradov Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk (VIG SB RAS). The reference samples from VIG SB RAS were previously certified only for their Au and Ag content, using several independent methods of graphite composition, whereas SOG-13 was certified as a reference material for Au, Ag and PGE by several independent methods (Catalogue of Reference Samples, VIG SB RAS, Irkutsk, 1988).

The calibration sample SOG-21-1 was obtained by introducing solutions of compounds of certified elements into a matrix prepared from pure graphite powder, OSCh 8-4 GOST (All-Union state standard of the former USSR) 23463-79, with subsequent heating at a temperature of 500 °C in an argon atmosphere, followed by grinding and homogenisation. The calibration samples SOG-21-2 to SOG-21-5 were obtained by appropriate dilution of the sample SOG-21-1 using graphite powder.

A set of calibration samples representing micro-impurities collected on graphite (SOG-13) was prepared and certified by the RAL USU. This set was intended for the calibration of instruments and certification of measurements made by atomic absorption spectrometry. Sample SOG-13-1 was obtained by introducing solutions of elements and their compounds (excepting Ir, Os, Rh and Ru) into a matrix consisting of graphite powder that met the requirements of state reference samples 23463-79. This sample was subsequently dried, ground and homogenised. The elements Ir, Os, Rh and Ru were introduced into the graphite matrix in the form of finely divided powders (particle size 2-10 µm). The calibration samples SOG-13-2 to SOG-13-4 were obtained by the subsequent dilution of the sample SOG-13-1 using graphite powder. The Au, Ag, Pd, Ru and Rh content of the sample SOG-13-4 was 1 µg g^{-1}, that of Ir and Os was 1.5 µg g^{-1}.

For geochemical investigations, reference materials prepared from natural materials were used (Arnautov 1990). These samples included VP-2 and ZH-3 (copper-

Table 2.
Certified values and confidence limits of Au, Ag and PGE in the reference materials

Certified reference material	Element content (μg g^{-1})						
	Ag	Au	Ir	Pd	Pt	Rh	Ru
Cu-Ni sulfide ore (VP-2)	2.15 ± 0.37	0.27 ± 0.05	0.042 ± 0.04	6.63 ± 0.45	2.64 ± 0.34	0.36 ± 0.05	0.10 ± 0.01
Cu-Ni sulfide ore (ZH-3)	2.6 ± 0.9	0.12 ± 0.02	0.06 ± 0.01	5.64 ± 0.30	1.16 ± 0.11	0.66 ± 0.07	0.2 ± 0.02
Cubanite ore SOP-NRK-23-85	85.3 ± 8.5	3.85 ± 0.39	-	36.9 ± 3.7	7.55 ± 0.75	-	-
Concentration tailings (HO-1)	0.58 ± 0.07	0.07 ± 0.02	0.010 ± 0.001	0.84 ± 0.02	0.43 ± 0.09	0.96 ± 0.04	0.029 ± 0.013

Uncertainties expressed as 95% confidence limits.

nickel sulfide ores), SOP-NRK—23-85 (cubanite ore) and HO-1 (tailings concentrate). The content of the platinum-group elements, gold and silver in these reference materials was certified by specialists in the geochemistry of the noble metals at different laboratories of the former USSR. Different methods were used: atomic absorption, emission spectral analysis after preconcentration and mass spectrometry. Certified concentration values are listed in Table 2.

In addition, reference materials of mineralogical materials prepared at the VIG SB RAS (Irkutsk) were also used for the investigation. These samples have also been certified for their gold and silver content using several independent methods.

Floatation concentrate of gold-bearing ore (SZK-3)

This concentrate is a typical product of flotation of a gold-bearing ore having a relatively low gold content. Certified elements are homogeneously distributed in this sample. The certified values and confidence limits (μg g^{-1}) are as follows: Au 34 ± 1, Ag 5.7 ± 0.3.

Gold-bearing ore (SZR-2)

The quartz sulfide gold-bearing ore is representative of sedimentary rocks (shales, siltstones, sandstones) with quartz veinlets and sulfide phenocrysts. The certified values and confidence limits (μg g^{-1}) are as follows: Au 4.6 ± 0.2, Ag 1.1 ± 0.1.

Gravitation floatation tailings of gold-bearing ore (SZH-4)

This reference material consists of a gold bearing ore, enriched by the floatation process. The certified values and confidence limits (μg g^{-1}) are as follows: Au 1.6 ± 0.2, Ag 0.53 ± 0.06.

Library of spectral lines

The spectrum of a two-jet plasmatron plasma differs significantly from that of direct or alternating current arcs (Yudelevich *et al.* 1984, Cherevko *et al.* 1988, Smirnova *et al.* 1997). This observation essentially limits the possibility of using currently available atlases and tables of spectral lines for interpretation of spectra. As a consequence, establishing a library of spectral lines for the noble metals and associated rock or ore forming elements was undertaken. This library covers almost all the elements in the periodic table. The basis of this library was the well known atlases of spectral lines of Harrison (1939), Zeidel (1977), Kalinin (1965), Rusanov (1958) and Arnautov (1987). In addition, account was taken of the spectral line tables of Boumans (1981) and Parsons *et al.* (1980), which list the most sensitive analytical lines in the argon inductively coupled plasma and also possible overlap interferences. In the library developed as part of the present study, there are one hundred or more spectral lines for every element investigated over the wavelength range used, including overlap interferences of associated elements found in ores and rocks. For each spectral line, the following characteristics are listed: excitation energy, ionisation degree, relative intensity on Zeidel's (or Kalinin's) scale, sensitivity and detection limit for the principal analytical lines based on the procedures described here. Spectral overlap interferences can significantly distort analytical results. By measuring several lines of an element simultaneously, the reliability of the determination can be improved and any bias caused by a spectral overlap interference can be identified and eliminated. Analytical measurements obtained by integrating the area delimited by the line contour, instead of by measuring the line intensity corrected for background, provides a way of improving the reliability of determinations and reducing the detection limit for gold, silver and the platinum-group elements. For example, in Figure 2, the contour of the Ag (I) line at 328.068 nm is given. By integrating the area by this

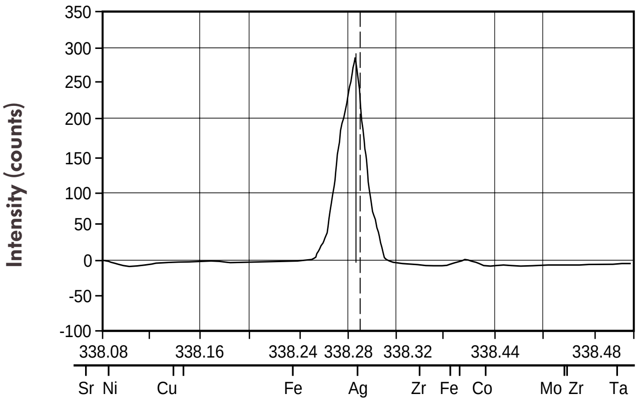

Figure 2. Spectral scan showing the peak shape of the Ag I 338.289 nm line.

analytical signal, determinations of Ag can be extended from 10 µg g^{-1} down to 0.01 µg g^{-1} whilst retaining a linear calibration response throughout the concentration range.

Construction of calibration curves and estimation of the detection limits

The detection limit ($I_{min,P}$) is equivalent to the minimum analytical signal and can be determined from the relationship in equation 1:

$$I_{min,P} = I_{contr} + \upsilon_p s_{Icontr} + \upsilon_p s_{Imin} \quad (1)$$

where I_{contr} is an analytical signal at the control experiment (e.g. blank spectrum), s_{Icontr} and s_{Imin} are standard deviations relevant to measuring the analytical signal in the control spectrum and the spectrum containing the analyte at the detection limit level, and υ_p is the coefficient appropriate for the selected confidence interval, P. Because of the different nature of control and sample spectra, the s_{Icontr} value is not necessarily equal to the s_{Imin} value, but when an analytical line is absent in the control experiment, it may be assumed that $s_{Icontr} = s_{Imin}$. In this case, $I_{min,P} = I_{contr} + 2\ \upsilon_p\ s_{Icontr}$. If the confidence interval is taken as P = 0.95 and $\upsilon_p = 2$, then the detection limit can be determined from equation 2:

$$I_{min,P} = I_{contr} + 4\ s_{Icontr} \quad (2)$$

The values of I_{cont} and s_{Icontr} can be determined from experimental measurements. For this purpose, fifteen to twenty spectra from the control experiment (i.e. graphite powder) and fifteen to twenty parallel determinations of each standard sample were recorded. The algorithm for the construction of calibration curves and determination of detection limits can be summarised as follows:

(1) For each parallel determination I/I_{ref} was calculated for the linear scale or $\log(I/I_{ref})$ is calculated for the logarithm scale of intensities, where I is the line intensity, as follows (equation 3):

$$I = I_{line\ +\ background} - I_{background} \quad (3)$$

where $I_{line\ +\ background}$ is the maximum amplitude of the analytical signal, $I_{background}$ is the minimum value representative of a continuous spectrum and I_{ref} is the intensity of a reference element line. If a reference element line is not used, $I_{ref} = 1$.

(2) For each group of reference samples and spectra of the control experiment, the average value $(I/I_{ref})_{mean}$ or $(\lg(I/I_{ref}))_{mean}$ was calculated from all parallel determinations of this group. The rejection of gross errors was undertaken. A deviation from the average value of no more than $\beta S_r I_{mean}$ was considered to be acceptable, where S_r is the relative standard deviation, and for P = 0.95 and N = 15-20, $\beta = 2.6$. After the elimination of outliers, s_I and $s_{I\ contr}$ were calculated. A check was undertaken for the homogeneity of selective dispersion using Kochren's or Bartlet's criterion.

(3) The coefficient of regression was estimated, depending on the chosen scale and calibration function. We used the relation: $\log I = a_0 + a_1 \log c$.

(4) The method of least squares was used to calculate the regression curve for the best fit of reference sample concentration to the mean calculated intensity in the chosen co-ordinate system.

(5) The adequacy of the resultant regression equation was estimated using the F-criterion. Values were calculated for the following parameters (Nalimov 1960, Doerfel 1969, Orlov 1986):

(a) dispersion of the convergence:

$$S_{con}^2 = [(n_1 - 1)\ S_1^2 + ... + (n_m - 1)\ S_m^2]\ /\ (N - m) \quad (4)$$

(b) dispersion of the adequacy, determining the dispersion of deviation of calculated data from experimental results:

$$S_{ad}^2 = [n_1\ (Y_{1mean} - Y_{1calc})^2 + ... + n_m\ (Y_{m,\ mean} - Y_{m,\ calc})^2]\ /\ (m - k) \quad (5)$$

where $Y_{i\ mean}$ is the mean value of the i^{th} group to be determined, Y_{1calc} is the calculated value of the same group from regression equation. The dispersion ratio was then calculated from:

$$F_{calc} = S_{ad}^2 / S_{conv}^2 \qquad (6)$$

If $F_{calc} < F_{tabl}$ (P, m - k, N - m), then the calibration curve was considered to be valid.

(6) The standard deviation of the calibration function was calculated using the relationship:

$$s_{calibr} = \{[(m - k)\, S_{ad}^2 + (N - m)\, S_{conv}^2] / (N - k)\}^{1/2} \qquad (7)$$

(7) The fiducial interval of the regression curve was calculated from the relationship:

$$d\,(Y_{calc}) = \pm\, t\,(P, N - k)\, s_{calibr}\, \{1 + 1/N + (x_i - x_{mean})^2 / \Sigma\, [(x_i - x_{mean})^2]\}^{1/2} \qquad (8)$$

where Y_{calc} is the calculated value of the s regression curve at the point x, t (P, N - k) is the value of the Student's distribution for the fiducial probability P (0.95 or 0.99 were used) and for the number of degrees of freedom f = N - k; x is the argument value: x = c or log (c) depending whether a linear or logarithmic scale was used; x_i is the value of i^{th} group of reference samples using the same scale; x_{mean} is the mean value of x for the reference samples with regard to the number of determinations made in the group:

$$x_{mean} = [n_1\, x_1 + \ldots + n_m\, x_m] / (N) \qquad (9)$$

(8) For control spectra, the mean value I_{contr} was calculated, following the rejection of gross outliers. From the calibration curve, the value c_{min} corresponding to the analytical signal $I_{min,P} = I_{contr} + 4\, s_{I\ contr}$ was found. The programme allowed the least determined value of concentration, i.e. the detection limit, to be calculated only for a linear calibration curve.

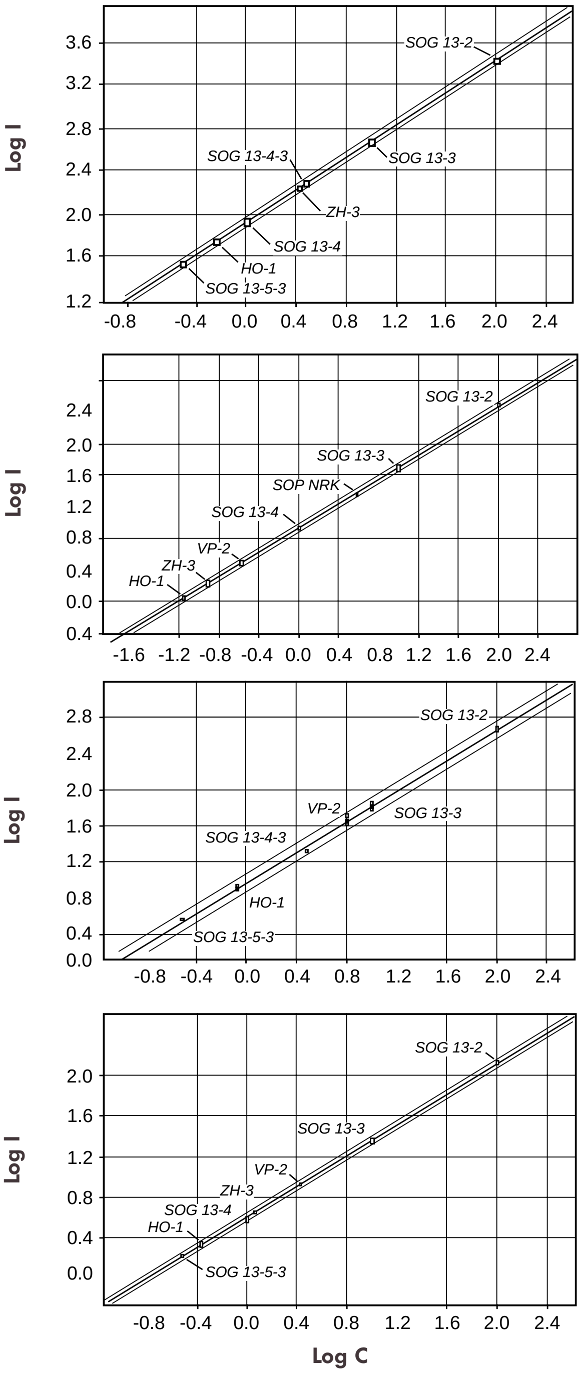

Figure 3. Examples of calibration curves (concentrations of elements in the reference samples are given in the text), for the following element lines: (1) Ag I 338.289 nm, (2) Au I 267.595 nm, (3) Pd I 342.124 nm and (4) Pt I 265.945 nm.

Results and discussion

In Table 3, parameters for the calibration curves for gold, silver and the platinum-group elements are listed. As can be seen, the slope of the linear calibration line for the most sensitive analytical lines is about 35-40° providing good sensitivity for analytical measurements. The small values of the "dispersion of the convergence" and the "adequacy" indicate that determinations can be made with sufficiently high precision. In Figure 3, calibration curves are plotted, on which the 95% confidence interval of determination of concentrations is shown. The high temperature of the plasma and chosen conditions of analysis result in a substantial decrease in the effect of sample matrix on the intensity of spectral lines. As can be seen from Figure 3, all

Table 3.
Parameters of calculation curves for gold, silver and platinum-group elements (P = 0.95)

Element	Wavelength λ (nm)	Parameters of calibration curves log I = a_o + a_1 log c			Checking uniformity of chosen dispersions against criterion (Orlov 1986)				Dispersions of:	
		a_0	a_1	α^0	Kochren G(P,m) tabular	calculated	Fisher (P,m-k,N-m) tabular	calculated	convergence S_{conv}^2	adequacy S_{ad}^2
Ag	I 338.289	1.925	0.766	37.4	0.43	0.32	2.91	0.81	0.0004	0.0003
	I 328.068	1.678	0.657	33.3	0.51	0.37	2.85	1.35	0.0002	0.0003
Au	I 267.595	0.915	0.772	37.7	0.50	0.35	2.56	2.38	0.0009	0.0021
	I 312.278	0.669	0.710	35.3	0.40	0.26	2.62	0.59	0.0016	0.0009
Ir	I 263.971	0.398	0.567	29.5	0.90	0.85	-	-	0.0022	0.0001
	I 292.479	-0.010	0.830	39.7	0.82	0.68	4.76	0.50	0.0096	0.0005
Os	I 248.555	-0.090	0.956	43.7	0.77	0.52	4.74	3.00	0.0018	5×10^{-5}
	I 283.869	-0.190	0.910	42.5	0.87	0.43	8.84	7.70	0.0005	0.0070
	I 290.906	0.380	0.790	38.4	0.59	0.46	3.86	2.04	0.0016	0.0030
Pd	I 324.270	1.050	0.830	39.7	0.44	0.30	2.80	0.49	0.0007	0.0003
	I 342.124	0.970	0.840	40.0	0.61	0.48	3.26	2.47	0.0013	0.0032
Pt	I 265.945	0.764	0.685	34.4	0.73	0.68	4.07	1.98	0.0006	0.0012
	I 306.471	1.299	0.682	34.3	0.64	0.60	3.86	2.45	0.0005	0.0012
Rh	I 339.685	0.547	0.853	40.5	0.78	0.62	5.14	1.60	0.0012	0.0020
	I 343.489	1.040	0.731	36.2	0.83	0.68	8.06	4.76	0.0014	0.0026

Table 4.
Verification of accuracy by the spike recovery method

Sample	Au I 267.595 nm			Au I 312.278 nm			Pd I 324.27 nm			Pd I 342.124 nm		
	C_{rs}	C	% RSD	C_{rs}	C	% RSD	C_{rs}	C	% RSD	C_{rs}	C	% RSD
SOG 13-2	100	106	4	100	109	4	100	97.7	5	100	105	5
SOG 13-4-3	3	2.94	5	3	2.87	7	3	3.12	9	3	2.95	15
SOG 13-4	1	1.07	8	1	1.01	4	1	0.971	9	1	1.01	15
HO-1	0.07	0.075	4	0.07	0.076	9	0.84	0.85	4	0.84	0.83	6

C_{rs}	certified value of the element concentration in the reference material (µg g^{-1}).
C	concentration determined from the calibration curve (µg g^{-1}).
% RSD	relative standard deviation of determination (%).

reference samples show a good fit to the linear calibration curve in spite of significant differences in matrix composition. This indicates that a range of different rocks and ores can be analysed against a single set of calibration samples.

The accuracy of the analytical procedure was verified by comparing analysed measurements with certified values for the reference materials studied here, as shown in Table 4. The relative standard deviation (RSD) does not exceed 15, but for most determinations, the RSD is as low as 4-6, when expressed as a mass fraction. When several analytical lines are used for the determination of an individual element, the precision of determination is substantially improved and also offers the benefit in some cases of identifying and eliminating bias in determinations from particular lines caused by spectrum overlap interferences (Zayakina 1999a, b).

Following optimisation of excitation and other instrumental conditions, we have developed a procedure for the determination of gold, silver and the platinum-group elements in sulfide rocks. The detection limits of this procedure are: Ag, Pd, Ru, Rh: 0.1 to 0.4; Au, Os: 0.07 to 0.09 and Pt: 0.5 µg g^{-1}.

In order to further demonstrate the accuracy of our method, we compared determinations with those by the atomic absorption technique on geological samples with weighted mean level contents of Au, Ag and PGE. A determination at such low concentrations is only possible by using extraction and preconcentration techniques. Following extraction and preconcentration of Au, Ag and PGEs from these geological samples, atomic absorption determinations were performed by V.G. Tsimbalist using a previously developed method (Tsimbalist *et al.* 2000). The extracted aliquot was divided into two equal parts.

Table 5.
Comparison of weighted mean concentration (C) of Au and Ag in selected sample types by dual arc plasmatron atomic emission (present work) and AAS

Sample	**Au**				**Ag**			
	PAE		**AAS**		**PAE**		**AAS**	
	C (μg g^{-1})	**% RSD n = 10**	**C (μg g^{-1})**	**% RSD n = 3**	**C (μg g^{-1})**	**% RSD n = 10**	**C (μg g^{-1})**	**% RSD n = 3**
Metabasalts	0.019	7	0.024	12	0.037	10	0.033	12
	0.130	9	0.130	10	0.083	10	0.086	15
Metadacites	0.080	10	0.065	15	0.061	15	0.080	10
	0.023	9	0.021	10	0.05	10	0.053	10
Metatuffs	0.046	10	0.032	15	0.032	10	0.032	8

PAE Dual arc plasmatron atomic emission (this work).

Table 6.
Detection limits for plasma atomic emission analysis

Element and ionisation degree	**Wavelength l (nm)**	**Detection limit (μg g^{-1})**	**% RSD**
Al (I)	308.215	0.03	12
Al (I)	309.284	0.03	12
B (I)	249.773	0.007	11
Bi (I)	306.772	0.04	15
Cd (I)	228.802	0.01	10
Cr (II)	267.716	0.02	12
Cr (II)	284.325	0.02	12
Cu (I)	324.754	0.04	12
Cu (I)	327.396	0.04	12
Fe (II)	259.837	0.02	15
Fe (II)	259.940	0.02	15
Ga (I)	294.364	0.01	15
Mg (II)	280.270	0.02	15
Mg (I)	285.213	0.02	13
Mn II	257.610	0.01	10
Ni (I)	300.363	0.01	15
Pb (I)	283.307	0.1	15
Sb (I)	252.853	0.15	15
Sn (I)	283.999	0.05	15
Te (I,II)	238.576	0.1	15
Tl (I)	255.253	0.1	15
Tl (I)	276.787	0.1	15

Detection limits calculated at $P = 0.95$, $I_{min,P} = I_{cont\ r} + 4\ s_{Icontr}$ (see text for details).

In the first part, Au, Ag and the PGE were determined by the atomic emission method described here using the automatic procedures described above. The extract was dried on graphite powder before analysis. Gold, Ag and PGE contents were determined using calibration plots, making use of the concentration coefficients Kc. When Kc = 100, it was possible to make determinations to detection limits than were two orders of magnitude lower than those for the direct method. The relative standard deviation (expressed as a mass fraction) for ten replicate determinations did not exceed 0.1. The results are presented in Table 5.

The second extraction aliquot was transferred into solution and analysed for Au, Ag and the PGE by the atomic absorption method, using a Perkin-Elmer 3030 AA spectrometer with a HGA-600 graphite atomiser. Background corrections were made using either the Zeeman effect or a deuterium lamp source. Results of this comparison are shown in Table 5, which shows that the accuracy of Au and Ag determinations by the developed method is comparable with the accuracy of the atomic absorption determinations.

We have also studied the possibility of the simultaneous determination of Au, Ag and the PGE together with a large number of associated elements. Detection limits were estimated from twenty replicate determinations following the procedure described above and are listed together with relative standard deviations in Table 6.

Conclusions

A valuable application of the argon arc two-jet plasmatron incorporating a multichannel MAES-10 analyser has been demonstrated. The high plasma temperature and carefully optimized conditions allow improved detection limits to be achieved as well as low matrix effects on the intensity of spectral lines. This allows analysis of various rocks and ores to be performed using a single set of calibration samples. Calibration curves for gold, silver and the platinum-group elements have linear slopes over a wide concentration range. Small values of dispersions of the convergence allow determinations to be made with a sufficiently high precision. Using several analytical lines for the determination of a single element improves the precision of determination and in some cases allows bias in determinations from an individual line caused by spectrum overlap interferences to be identified and eliminated.

A procedure allowing the simultaneous determination of gold, silver and the platinum-group elements has also been developed, offering detection limits down to 0.1 $\mu g\ g^{-1}$. As a further development of the method, the authors envisage using a combination of direct atomic emission spectrometry with a scintillation method of spectral analysis, which may offer an even more promising method for the determination of Au, Ag and the PGE and other ore-forming elements that occur in individual minerals in geological samples.

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