THE STUDY OF DRIFT IN INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY. ANALYSIS OF SILICATE AND CARBONATE RAW MATERIALS

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The work shows the importance of maintaining a constant temperature in a spray chamber to obtain a stable signal in the ICP spectrometry of water solutions. Simple shielding against ICP thermal radiation and forced air circulation in a plasma torch/spray chamber housing have been proposed and used instead of a double-wall temperature-controlled spray chamber. The internal standard method has been used to improve signal stability. The number and composition of calibration solutions have been optimized for the determination of the main constituents of some silicate and carbonate raw materials. An ultrasonic cleaning bath has been successfully used instead of stirring to dissolve the samples after fusion with $LiBO_2$. Certified Czech and Slovak geological reference materials and some international standards have been used to test the accuracy. Statistical tests have proved that the method of determination complies with the requirements of technological standards.

ICP-OES is now frequently used in the analysis of geological samples and raw materials for the building, ceramic and glass industries for its known advantages. Many papers have been published on the determination of Si, Al, Ca, Mg, K, Na, Fe, Ti, Mn and P, e.g.: in silicate rocks[1 – 3], carbonate rocks[4,5], phosphate rocks[6] and in slags[7]. The utmost repeatibility and accuracy are required for the determination of the main constituents. Calibration solutions do not match the samples precisely and, therefore, significant systematic errors (2 – 3 rel.%) occure due to their different properties. Moreover, instrumental drift worsens the results.

Improved signal stability and accuracy can be achieved using an internal reference method (IRM) to minimize measurement fluctuations and small matrix effects[8 – 15]. However, IRM, based on a simple ratio of intensities of analyte and reference lines, does not fully remove drifts. Therefore, a generalized internal reference method (GIRM) has been developed[16,17], based on the correlation of the analyte intensity with the power function of the intensities of one or more internal reference lines reflecting fluctuations of the individual plasma parameters. The parameter-related internal standard method (PRISM) has been developed to minimize both systematic and random errors caused by a combination of "mini-matrix effects" and drifts[2].

Many factors influence the stability of the signal generated in the ICP discharge, namely the temperature of the spray chamber is important, especially in the case of organic solvents[16 – 20]. Neverthless, the influence of temperature on the generation and transport of an aerosol and on the load of the plasma with vapour and condensed phases could also be observed in water solutions.

The aim of this work was to find an extremely reliable, universal and simple method for the determination of the main constituents in silicate and carbonate raw materials using IRM and to evaluate the influence of temperature changes in the spray chamber on the behaviour of the analyte-to-reference lines ratio. A simple IRM was used instead of GIRM because of limited equipment.

EXPERIMENTAL

Chemicals and Solutions

Single-element stock solutions 1 mg ml^{-1} MgO, Fe_2O_3, TiO_2, MnO, Na_2O, 5 mg ml^{-1} CaO and 0.5 mg ml^{-1} Cd (internal standard) were prepared from chemicals of analytical grade purity. Silica (Silquartz special, Rudné doly Jeseník, The Czech Republic) was purified with HCl, alumina and calcium carbonate were of analytical grade purity (Lachema Brno, The Czech Republic). Lithium metaborate for the fusion was Spectromelt A 20 (Merck, Germany).

Preparation of Sample and Calibration Solutions

Samples were dissolved according to standard procedures[3,21]. The sample (0.25 g) was mixed in a platinum crucible with 0.75 g of $LiBO_2$ and fused for 20 min. The resulting glass bead was allowed to cool and then the crucible was immersed in a polythene beaker (150 ml) containing 100 ml of 0.7 M HNO_3 and 25 ml of the internal standard stock solution. After electromagnetic stirring (1.5 h) with a teflon-coated stirrer, the resulting solution was transferred to a 250 ml volumetric flask, diluted with distilled water and stored in a polythene bottle. In some of the samples, an ultrasonic cleaning bath was used for the dissolution, however, as the time requirement was approximately the same, 15 samples could be treated simultaneously.

The above procedure was used successfully for the decomposition of limestone, marly limestone, dolomite, and the other materials given in Table I. Both sample and calibration solutions were proven to be stable for at least three months.

Calibration solutions were prepared using the fusion of SiO_2, Al_2O_3 and $CaCO_3$ with $LiBO_2$ followed by addition of the stock solutions. The silica and alumina were ignited, the $CaCO_3$ was dried and then they were weighed precisely and fused with $LiBO_2$ for each of the calibration solutions individually. All other elements were added from the stock solutions.

Although pure $CaCO_3$ is readily soluble in acids, the fusion with $LiBO_2$ without a preliminary acid dissolution has been employed both for the preparation of the calibration solutions and for the limestone samples. There are two reasons for this procedure.

First, the routine preparation of sample solutions (80 samples per one shift) requires the same decomposition procedure even though the sample contains almost pure limestone, marly limestone or a mixture with a waste rock (silicates). Otherwise, the residues after the preliminary dissolution would have to be filtered, ashed and ignited, which would prolong and complicate the decomposition procedure.

TABLE I

Testing reference materials (RM) used for the evaluation of the repeatibility of measurement and the accuracy of determination

Name of RM	Symbol[a]	n[b]	Name of RM	Symbol[a]	n[b]
Bentonite	E6	39	Tonschiefer	TB[c]	41
Feldspatsand	FK[c]	17	Kaolin	E23	4
Illite-clay	E5	16	Na-K Feldspar	E8	4
Kaolin-clay	E4	26	Serpentinite	E20	4
Na-Ca Feldspar	E3	7	Dinas	8-2-05[d]	25
K Feldspar	E2	16	Quartzite	8-2-03[d]	10
Olivin. gabbro	E7	10	Kaolin Karlsbad	check[e]	4
Basalt	BM[c]	20			

[a] Identification symbol of RM from ref.[22]. [b] *n* Number of measurements. [c] International reference material (formerly COMECON standards), Zentral Geologisches Institut Berlin O-1040: FK Feldspathic sand, CMEA standard; BM CMEA No. 2300; TB Slate, CMEA No. 2301. [d] CSFR State analytical reference material, NH Steelwork Ostrava. [e] Laboratory check sample.

TABLE II

ICP spectrometer and operating conditions

Polychromator	Paschen–Runge, $r = 1.5$ m, 30 channels + 1 movable
illumination	source imaged (1 : 1) on the grating
grating	blaze 450 nm, $1/R = 0.555$ nm mm^{-1} (1st order)
SBW	28 pm in the 1st order (195 – 670 nm)
ICP generator	50 MHz, free-running, power 1 400 W
plasma torch	quartz, compact, type 36 Philips
Argon l/min	outer 18.3, intermediate 0.43, carrier 1.06
nebulizer	cross-flow, adjustable PTFE capillaries[a]
spray chamber	cylindrical, spherical spoiler[a]
pump	peristaltic, six-roller (Ismatec, France)
sample uptake	2.1 ml min^{-1}
observed zone	4 mm high, zone center 16 mm above the load coil
Measurement	two 10 s integrations, preflush 120 s/sample
Computer	P 855 M Philips, software CESPEC II

[a] Ref.[24].

Second, obtaining various amounts of residues from different limestone samples, one has to apply enough flux in order to maintain a sufficient excess over the maximum residue. The residue frequently represents 30% or more of the weight of the sample (marly limestone). Preliminary sorting of the samples based on the amount of loss on ignition enables to vary the amount of the flux, however, this leads to an increased number of calibration solution sets and hence to more frequent calibrating.

Instrumentation and Operating Conditions

PV 8210 simultaneous spectrometer with PV 8280 roving detector and the PV 8490 (Philips) ICP source, cf. Table II, AA 875 ABQ (Varian) atomic absorption spectrophotometer and UZV 12 (Tesla Vráble, The Slovak Republic) ultrasonic cleaning bath were used. The lines are given in Table III.

Reference Materials

Repeatibility of measurement and accuracy of determination were evaluated using the set of reference materials currently employed in the analytical laboratories of the Czech and Slovak geological institutes. These are listed in Table I together with their identification symbols[22] used in Table VII. Because of the large variety of tested reference materials, the results obtained using limestones and dolomites are not included in this paper.

RESULTS AND DISCUSSION

Optimization of Operating Conditions of the ICP Source

The optimization of the working parameters of this ICP source has been described for some elements in detail[23]. In our experiments, the relaxation method was also used. Power input, carrier gas flow rate, observation height and sample uptake rate were varied in order to obtain the maximum signal-to-noise ratio. For simultaneous multielement analysis, the optimum conditions found for Si, Al and for Ca, Mg lines were

TABLE III
Analytical lines (λ) and background equivalent concentrations (BEC)

λ, nm		*BEC*, mg l^{-1}	λ, nm		*BEC*, mg l^{-1}
Cd I	228.802[a]	0.5	Al I	308.215	2.6
Si I	251.617[b]	2.9	Ca II	315.887[b]	2.5
Mg II	280.270	1.4	Ti II	368.519	0.39
Mn II	293.930[b]	0.17	Na I	588.995[c]	0.60
Fe I	302.063[b]	2.6			

[a] The internal standard line. [b] The 2nd spectral order. [c] The line measured with a movable detector assembly.

preferred over the optimum conditions for other elements to attain the necessary repeatibility and accuracy of the determination of Si, Al and Ca, Mg in silicates and carbonates, respectively. However, the compromise conditions given in Table II do not differ greatly from the optimum ones for individual lines, except with Na. Due to the high concentration of dissolved sample, considerable memory effects (Si, Ca) were observed and, therefore, a preflush time between the samples was prolonged to 120 s from commonly used 60 s.

The expected depression (10%) of the net line intensities in the presence of 3 000 mg l^{-1} $LiBO_2$ was observed under the compromise conditions. This depression slightly changes (±2%) within the range from 2 000 to 4 000 mg l^{-1} $LiBO_2$.

Of the three examinated internal reference lines (Y II 371.030 nm, Cd I 228.802 nm and Co I 345.351 nm), cadmium yielded the closest linear correlation and the greatest decrease of relative standard deviation of the analyte-to-reference ratio in comparison with the relative standard deviations of the analytes[3].

Spectral interferences were not observed. A scattered light originating from Ca II 393 nm and Ca II 396 nm was eliminated using the interference filter (BRF Ca 395, Acton Research Corp.).

Effect of Internal Reference on the Drift Compensation

The function of the Cd line in the role of internal reference is shown in Fig. 1. Measurement began 30 min after plasma ignition. The relative intensities of Ca (curve *1*) and Cd (curve *2*) lines were calculated by dividing them with the first corresponding values (calibration). The ratio of the relative intensities is represented by the curve *3*. It is evident that some fluctuations common to both Ca and Cd line intensities are smoothed

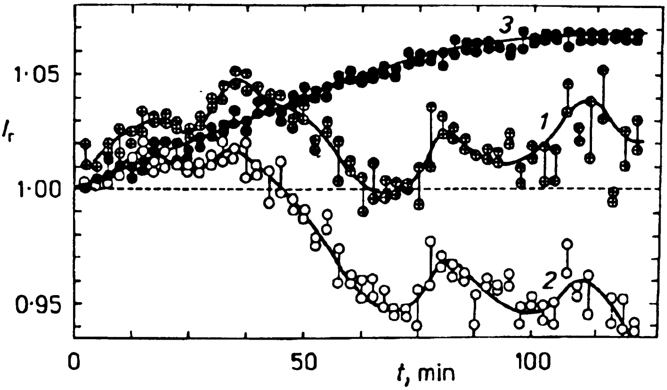

FIG. 1

Compensation of drift with internal reference line. *1* Intensity of Ca II 315 nm, *2* intensity of Cd I 228 nm, *3* ratio of intensities Ca/Cd, 2 points on one vertical: parallel integrations (Δt = 10 s) out by the IRM, however, a redundant drift represents the increase of this ratio by 7% during 2 h of operation. This increase exhibits the character of a temperature drift.

A temperature increase by 11 °C of the outer surface of the spray chamber was measured during the long-time ICP operation. This is a result of heating by both the plasma discharge and the oscillator tube. (The spray chamber is placed together with the plasma torch in the metal housing, which is close to the high frequency oscillator. Inside the housing, the plasma torch is shielded with a Faraday cage.)

This temperature drift is also evident from Fig. 2. The considerable decrease of the intensity of Ca II 315.887 nm (curve *2*) began after 105 min, when the ventilator fan which had been installed was started up. As a consequence, the air temperature in the torch/spray chamber housing dropped by 4 °C (curve *3*). However, this drift was partially compensated by the internal reference line Cd I 228.802 nm. The ratio of the intensities of Ca and Cd lines did not drop so sharply (curve *1*). The laboratory was air-conditioned, and this forced circulation of air maintained a practically constant temperature in the spray chamber. The influence of the temperature increase on the pressure drop Δp of the massive PTFE nebulizer was demonstrated by the one-hour delay (curve *4*). Neverthless, the drop of the Ca line intensity ($t > 105$ min) at the stabilized value of $\Delta p = 265$ kPa shows that the observed drift can not be ascribed simply to the variation in aerosol particle size distribution and to the variation of the ratio of the vapour/condensed phases entering and loading the plasma.

A steady state after half an hour's stabilization of the ICP discharge is shown in Fig. 3. The ventilator fan was in operation and the spray chamber was protected from thermal radiation with thermoinsulating baffles covered with reflecting Al foil. In spite

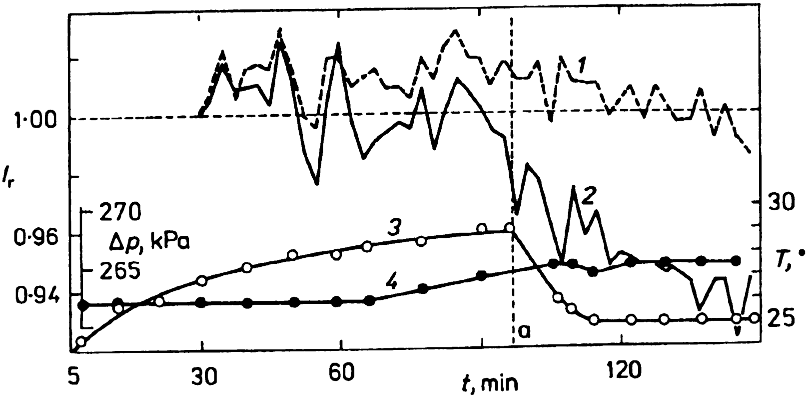

FIG. 2

Influence of temperature on analyte line intensity and on signal ratio of Ca/Cd. *1* Ratio of the intensities of Ca/Cd, *2* intensity of Ca II 315 nm, *3* temperature in the spray chamber/plasma torch housing, *4* nebulizer pressure drop, a air circulation started of high fluctuations in both signals (curves *1*, *2*) the Ca/Cd ratio exhibits less variability compared to that shown in Fig. 1.

Calibration and Recalibration

Linearity of calibration curves has been evaluated[3]. However, statistical treatment of a large number of routine analyses later revealed that systematic errors (approx. 2 rel.%) occured depending on matrix and concentration. Hence, routine samples were sorted into seven groups for calibration and recalibration (cf. Table IV).

New calibration curves were measured individually for each group. Their ranges were narrower than those in ref.[3] and two-point recalibration curves including a "low

TABLE IV
Types of samples and used recalibration solutions

Type groups of samples	Solutions[a]
1. Limestones (pure, marly)	1, 6
2. Dolomite	4, 6
3. Magnesian limestone	1, 4, 6
4. Limestone or dolomite with waste rock	3, 6, 7
5. Alumosilicate rocks	2, 3, 6
6. Ultrabasic ores	2, 3, 5
7. Quartzite and sands	8, 9

[a] The identification numbers of the recalibration solutions given in Table V.

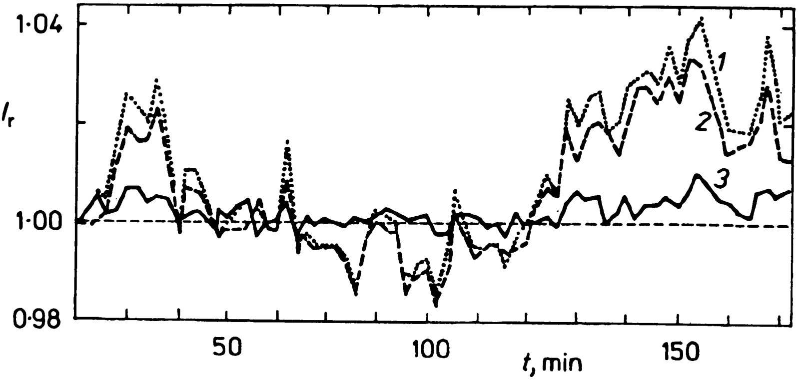

FIG. 3
Drift compensation using IRM under stabilized temperature in spray chamber/plasma torch housing. *1* Intensity of Ca II 315 nm, *2* intensity of Cd I 228 nm, *3* ratio of intensities Ca/Cd

point" (LP) and a "high point" (HP) were created. Nine recalibration solutions were sufficient to cover the seven types of samples (cf. Tables IV and V). One recalibration solution can include the HPs for some analytes and the LPs for others. The same recalibration solution can be used for several types of samples, cf. Table IV. Actual numbers of HPs (55) and LPs (49) differ from expected numbers (56 LPs and 56 HPs) for 8 elements and 7 groups of materials as one recalibration list is common for both limestone and magnesian limestone (solution No. 4). The recalibration concentrations were derived based on both the theoretical compositions of pure rocks and the values empirically found on routinely analyzed samples.

All calibration curves were linear except for Mg in the range from 10% to 40% of MgO (in ultrabasic ores). This curvature was solved using a segmented calibration curve consisting of 4 linear parts (chords).

Long-Term Repeatibility of Measurement

Long-term repeatibility of measurement was evaluated based on the sets of results obtained with the reference materials listed in Table I. These sets comprised from 4 to 41 results for each analyte. Data were measured both immediately after a recalibration and before the following one. The arithmetic mean and standard deviation were calculated with the results both following and preceeding the recalibration. This procedure assured a drift randomization between 2 recalibrations which were usually performed within half an hour, i.e. after the measurement of 10 routine samples and some reference samples. Data were accumulated during one week (five eight-hour shifts) and therefore,

TABLE V
Composition of recalibration solutions

Solution number	ρ, mg l^{-1}							
	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	Na_2O
1	560	0	0	0	0	0	0	0
2	0	0	800	400	0	0	0	0
3	140	100	450	150	100	40	10	50
4	300	250	0	0	0	0	0	0
5	0	400	400	0	0	0	0	0
6	350	70	200	70	30	2	5	5
7	300	0	300	0	0	0	0	0
8	0	0	1 000	0	0	0	0	0
9	50	20	750	100	100	5	2	5

the standard deviation characterizes the repeatibility of the one-week period. The number of results for each tested material is given in the column *n* in Table I.

The relative standard deviations of the long-term repeatibility of measurement, s_r, were calculated and plotted against the contents of the analytes in the solid samples. The earlier measured[25,26] and theoretically derived[27] hyperbolic courses of these dependences were obtained, e.g. for MgO, (cf. Fig. 4). The index of repeatibility (*r*) was calculated on the basis of the intralaboratory variance s_r^2 according to the norm[28]. Table VI contains these values for Al_2O_3 and CaO in silicate matrices. The constant s_r

TABLE VI

Dependence of the relative standard deviation of the repeatibility of measurement (s_r) on the content (*p*) of a constituent in a solid sample and corresponding values of the index of repeatibility (*r*)[a]

p, %	Al_2O_3		CaO	
	s_r, rel.%	*r*, %	s_r, rel.%	*r*, %
0.5	10	0.14	10	0.14
1.0	7.2	0.20	8.0	0.22
5.0	2.9	0.41	3.0	0.42
10.0	1.6	0.45	1.7	0.48
15.0	1.3	0.55	1.2	0.50
20.0	1.1	0.62	1.0	0.56
30.0	0.92	0.77	0.88	0.74

[a] Index of repeatibility[28] $r = 2.8\ s_r$ for the probability level 95%.

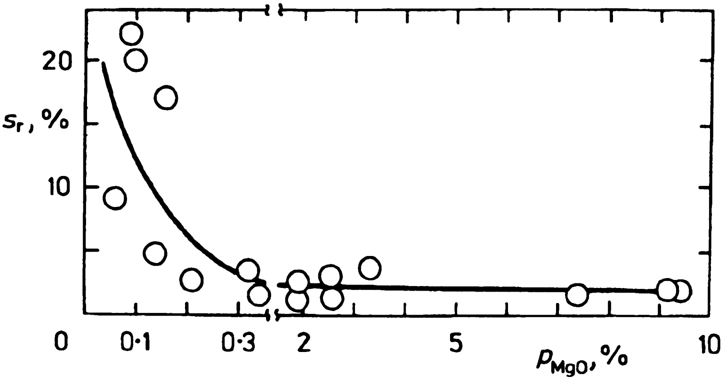

FIG. 4

Dependence of relative standard deviation of repeatibility of measurement (s_r) on the content of MgO in standard reference materials

Table VII
Accuracy of determination[a]

RM[b]	$p \pm s\ t/n^{0.5}$		RM[b]	$p \pm s\ t/n^{0.5}$	
	recommended	found		recommended	found
	SiO_2			Al_2O_3	
E20	39.71 ± 0.16	40.02 ± 0.15	8205	1.24 ± 0.03	1.18 ± 0.05
E6	45.20 ± 0.36	45.21 ± 0.33	E20	1.64 ± 0.07	1.54 ± 0.02
E4	47.24 ± 0.14	47.13 ± 0.13	FK	6.18 ± 0.04	6.15 ± 0.15
E7	49.47 ± 0.16	49.44 ± 0.29	E2	11.64 ± 0.09	11.48 ± 0.08
BM	49.51 ± 0.07	49.87 ± 0.19	E6	13.38 ± 0.16	13.32 ± 0.08
E5	54.66 ± 0.36	54.75 ± 0.29	BM	16.25 ± 0.10	16.07 ± 0.13
TB	60.23 ± 0.06	60.66 ± 0.07	E5	17.44 ± 0.14	17.78 ± 0.16
E3	61.97 ± 0.27	62.06 ± 0.44	E7	17.83 ± 0.06	17.96 ± 0.14
E8	73.29 ± 0.16	73.51 ± 0.52	TB	20.64 ± 0.08	20.56 ± 0.41
E2	78.64 ± 0.19	78.56 ± 0.53	E3	23.20 ± 0.15	22.96 ± 0.10
FK	88.2 ± 0.1	88.74 ± 0.69	E4	34.88 ± 0.16	34.93 ± 0.15
	CaO			MgO	
FK	0.11 ± 0.01	0.15 ± 0.03	E3	0.09 ± 0.01	0.09 ± 0.01
E4	0.28 ± 0.04	0.29 ± 0.05	E2	0.10 ± 0.01	0.09 ± 0.01
E2	0.31 ± 0.02	0.34 ± 0.02	FK	0.15 ± 0.01	0.17 ± 0.03
TB	0.33 ± 0.02	0.31 ± 0.02	E8	0.19 ± 0.04	0.16 ± 0.01
E8	0.65 ± 0.07	0.77 ± 0.02	E4	0.35 ± 0.02	0.33 ± 0.01
E5	0.96 ± 0.07	1.02 ± 0.04	TB	1.93 ± 0.04	1.93 ± 0.02
E20	1.62 ± 0.06	1.72 ± 0.07	E6	2.71 ± 0.12	2.80 ± 0.05
8205	3.81 ± 0.05	3.83 ± 0.10	E5	3.40 ± 0.15	3.61 ± 0.07
E3	4.76 ± 0.14	4.67 ± 0.15	BM	7.47 ± 0.05	7.51 ± 0.04
BM	6.47 ± 0.06	6.38 ± 0.04	E7	9.09 ± 0.04	9.20 ± 0.12
E6	8.94 ± 0.11	9.10 ± 0.07	E20	36.93 ± 0.21	36.99 ± 0.62
E7	10.50 ± 0.11	10.82 ± 0.13			

TABLE VII
(*Continued*)

RM[b]	$p \pm s \,.\, t/n^{0.5}$		RM[b]	$p \pm s \,.\, t/n^{0.5}$	
	recommended	found		recommended	found
	Fe_2O_3			TiO_2	
8203	0.25 ± 0.02	0.17 ± 0.01	E3	0.026 ± 0.004	0.023 ± 0.003
FK	0.26 ± 0.01	0.27 ± 0.03	E20	0.033 ± 0.002	0.029 ± 0.004
E2	0.36 ± 0.02	0.36 ± 0.02	FK	0.058 ± 0.005	0.059 ± 0.006
8205	0.76 ± 0.03	0.78 ± 0.03	E2	0.067 ± 0.005	0.073 ± 0.005
E3	0.86 ± 0.04	0.85 ± 0.03	E7	0.34 ± 0.02	0.33 ± 0.02
E4	1.37 ± 0.05	1.33 ± 0.05	8205	0.62 ± 0.03	0.63 ± 0.02
E20	6.89 ± 0.11	6.81 ± 0.12	TB	0.93 ± 0.02	0.92 ± 0.03
TB	6.90 ± 0.03	6.89 ± 0.07	BM	1.14 ± 0.02	1.12 ± 0.05
E7	8.03 ± 0.06	8.00 ± 0.06	E4	1.18 ± 0.09	1.17 ± 0.03
BM	9.67 ± 0.04	9.61 ± 0.07	E5	1.20 ± 0.03	1.19 ± 0.04
E5	9.89 ± 0.14	10.07 ± 0.07	E6	2.39 ± 0.04	2.42 ± 0.04
E6	12.31 ± 0.16	12.22 ± 0.10			
	MnO			Na_2O	
FK	0.0037 ± 0.0004	0.0028 ± 0.0005	E20	0.027 ± 0.007	0.026 ± 0.008
TB	0.052 ± 0.003	0.049 ± 0.001	E6	0.079 ± 0.006	0.080 ± 0.005
E20	0.12 ± 0.01	0.123 ± 0.002	E4	0.18 ± 0.02	0.19 ± 0.02
E7	0.12 ± 0.01	0.134 ± 0.001	E5	0.21 ± 0.01	0.20 ± 0.02
BM	0.140 ± 0.005	0.145 ± 0.007	FK	0.25 ± 0.01	0.24 ± 0.02
			TB	1.32 ± 0.03	1.21 ± 0.01
			E2	1.50 ± 0.03	1.52 ± 0.04
			E7	2.76 ± 0.08	2.69 ± 0.09
			E8	4.39 ± 0.07	4.43 ± 0.08
			BM	4.65 ± 0.05	4.71 ± 0.17
			E3	7.79 ± 0.15	7.72 ± 0.20

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[a] Confidence interval on the probability level 95%; t Student's coefficient, s standard deviation, n number of observations: for found values given in Table I, for recommended values: for Czechoslovak RMs $n = 7$, for ZGI (COMECON) RM n differs for various elements and RMs n is between 17 and 58. [b] Reference material.

was observed for contents higher than 2% SiO_2, 10% Al_2O_3, 5% CaO, 0.3% MgO, 0.1% TiO_2, 2% Fe_2O_3, 1% NaO and 0.05% MnO at 0.1% concentration of the analyzed solutions. In the area of the constant s_r the repeatibility of measurement is characterized with s_r between 1 and 2 rel.%. As the recommended values of results[22] used for statistical evaluation were not obtained using the ICP-OES technique, the repeatibility of the method could not be evaluated.

Accuracy of Determination

No significant differences between parallel decompositions of the reference samples were found. The measurement itself was the main source of random variability of the results. Recommended values were compared with interval estimates found using the described method, (cf. Table VII) and the accuracy was tested using the Student's test[29] and with orthogonal regression[30]. Testing procedures yielded a high level of agreement with the recommended ones. The most of the tolerances of various classes of technological materials were maintained[31].

Limits of Quantitative Determination

The value of the content of an analyte in a sample with a relative standard deviation of 10% is generally considered as the limit of quantitative determination[32]. These values were derived from the plots of the dependences of the relative standard deviations of determination against the contents of the analytes in reference samples. The values are valid for silicate matrices and are expressed in percentage for a solid sample: 0.50 CaO, 0.10 MgO, 0.50 Al_2O_3, 0.30 Fe_2O_3, 0.060 TiO_2, 0.010 MnO and 0.10 Na_2O.

CONCLUSION

The temperature drift of the spray chamber and nebulizer was found to be the most significant source of the drift of analytical signals. The IRM partially compensates the fluctuations of signals, however, the variation of the ratio of intensities caused by the temperature drift is not completely eliminated. We minimized this drift and increased the efficiency of the IRM by insulating the spray chamber with reflecting baffles and using the forced exchange and circulation of air in the plasma torch/spray chamber housing. This technical improvement is simpler than using a double-wall spray chamber connected to a water thermostat.

The ultrasonic dissolution of the melted samples proved to be efficient and space-saving. The number and composition of calibration solutions can be optimized so that a wide variety of materials can be analyzed using one method. The reliability of the proposed method was tested using geological reference materials with a high degree of consistency.

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