Solid Sampling in Analysis of Soils by Two-jet Plasma Atomic Emission Spectrometry

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The possibility of direct analysis of soils by two-jet plasma atomic emission spectrometry was investigated using certified reference materials of black earth, grey desert and red soils. It was shown that As, B, Cd, Cu, Hg, P, and V could be determined after a 2-fold, and Be, Co, Cr, Ga, Nb, Pb, and Zn—after a 10-fold dilution of the samples by a spectroscopic buffer using calibration samples based on graphite powder. The strongest matrix effects were revealed for red soil having the highest Al and Fe concentration, which led to the overstated concentrations of some elements. The overstating factor depended on analyte concentration and was no more than 2. A clear advantage of the suggested technique over existing methods is the simple sample preparation process, which requires no reagents except a spectroscopic buffer, and possibility of using the same calibration samples for analysis of different soils.

Keywords Two-jet plasma, soil, trace elements, matrix effects, graphite powder

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Introduction

The growing social concern for environmental protection and human health has sparked a widespread interest in trace element research in the various environmental compartments in the last decades. The amount of potentially hazardous trace elements dispersed in the ecosystem is considerable, and the anthropogenic inputs are breaking the natural biogeochemical cycles of trace elements on the Earth.[1] Among the most harmful contaminant trace elements are As, Cd, Cr, Cu, Hg, Pb, Zn, and several others.

Nowadays, many analytical methods are employed for soil analysis,[2] and inductively coupled plasma atomic emission spectrometry (ICP-AES) is most widely used. To extract elements from soil into solution, sample digestion in different acid mixtures composed of HF, HCl, HNO_3, $HClO_4$, and H_2O_2 is applied.[3-6] Complex matrix composition of soils often complicates trace element determinations due to spectral interferences. To exclude spectral overlapping, Picoloto *et al.*[7] developed a method for As, Cd, Hg and Pb volatilization from soil using microwave-induced combustion. Such a matrix separation allows for low limits of detection (LODs) of these elements.

Wet acid digestion of soils may result in element losses due to incomplete dissolution of the sample or element volatilization. In addition, the acids used are rather harmful and their application results in unhealthy working conditions when a great number of the samples are analyzed. It is contrary to the concept of green analytical chemistry, and solid sample preparation appears to be more preferable from this point of view. X-ray fluorescence,[8-10] neutron activation analysis,[11,12] and laser induced breakdown spectroscopy[6,13,14] are applied for direct analysis of soil in the form of pellets or powders. However, these methods are used not as often as ICP-AES due to the considerable matrix effects and require the calibration samples similar to the analyzed ones. Lack of soil CRMs of a different nature containing many elements in a wide range of concentrations complicates the application of these methods for multielemental analysis of soils.

A two-jet plasma (TJP) presented in this work is a high-power excitation source for atomic emission spectroscopy. The TJP is a direct current plasma (DCP) designed at the Kyrgyzstan Institute of Physics in the mid-70s. The power of TJP was 10 - 15 kW while ICP and DCPs[15,16] developed about at the same time had a power by an order of magnitude lower than the TJP. High power allowed using the TJP for direct analysis of powdered samples.[17]

Applying the TJP makes it easier to solve the problem of calibration samples in analysis of different powders than in the above methods used for solid sample analyses. Earlier, it was shown that the same calibration samples based on graphite powder could be used for direct TJP-AES analysis of both high-purity substances[18,19] and various biological samples[20-22] after dilution of the sample by a spectroscopic buffer. This fact denotes the comparatively weak matrix effects in the TJP, which are partially caused by a weak plasma temperature dependence on matrix composition.[23] Unlike biological samples and high-purity substances, the mineral composition of soils is complex and varies within a wide range, which can complicate using this approach for soil analysis. The aim of this work was

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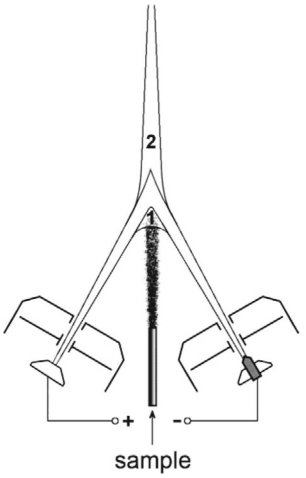

Fig. 1 Plasma torch and analytical regions: 1, before the jet confluence; 2, after the jet confluence.

to study the behavior of anthropogenic and other elements in various soils and estimate the possibility of their direct determination by TJP-AES using calibration samples based on graphite powder. The new modernized plasmatron recently developed was employed in the present work.

Table 1 Working conditions of the two-jet plasma

Parameter	Value
Current strength	85 A
Voltage	120 V
Plasma gas flow	4 L min^{-1}
Carrier gas flow	0.85 L min^{-1}
Angle between the jets	60°
Observation zone	4 - 5 mm lower than the point of the confluence

Table 2 Matrix composition of soil CRMs (wt%)

	SKR (red soil)	SSK (grey desert soil)	SCT (black earth)
SiO_2	59.18	52.65	71.49
TiO_2	1.56	0.64	0.74
Al_2O_3	17.01	11.48	9.81
Fe_2O_3	7.86	4.60	3.48
MnO	0.051	0.089	0.079
CaO	0.17	11.47	1.60
MgO	0.92	2.99	0.95
K_2O	0.98	2.09	2.42
Na_20	0.15	1.64	0.81
P_2O_5	0.10	0.17	0.18
C/organic	2.1	0.2	2.4
CO_2/carbonate	0.2	8.9	0.2

Experimental

Plasmatron

A high-power two-jet arc plasmatron designed at "VMK-Optoelektronika" (Russia) was used. Argon plasma jets were generated in two units with non-consumable electrodes (tungsten cathode and copper anode) connected to power supply, gas delivery, and water cooling systems. The jets joined at the output to form an arc plasma discharge (Fig. 1). The power supply system of the plasma generator fabricated using state-of-the-art solid state components, the gas flow control and automatic sample introduction systems were computer controlled. The TJP power can be modified from 5 to 12 kW by changing the current strength in the range of 40 - 100 A. Current fluctuation does not exceed 1%.

A Grand spectrometer[24] equipped with a concave diffraction grating (2400 lines/mm) and two multichip photodiode arrays, which were a key component of a multichannel analyzer of emission spectra (MAES), allowed spectrum registration in two spectral ranges: 185 - 350 and 385 - 470 nm. The MAES system is supplied with ATOM software package, which allows spectral data processing: measurement of analytical signals with background correction, construction of calibration curves and calculation of element concentrations.

A powder-introduction device was employed to transfer the powders into the plasma. A 20-mg sample placed into a Plexiglas beaker was inserted into the device where a spark between zirconium electrodes over the surface of the powder initiated blast waves agitating the powder. A resulting aerosol was delivered into the plasma with a carrier gas. The operating parameters of the TJP are presented in Table 1.

Materials and sample preparation

For developing the technique, the soil certified reference materials (CRMs)—red soil (SKR), grey desert soil (SSK), and black earth (SCT)—were applied (Table 2). Two or three samples of each kind of soil with different content of anthropogenic elements were at our disposal. In addition, four samples of artificial CRM "Granite-10" containing different concentrations of elements were used. Matrix composition of "Granite-10" is the following: SiO_2, 70; Al_2O_3, 17; CaO, 4; Na_2CO_3, 4; Fe_2O_3, 3; and MgO, 2 wt%.

For analysis, 100 mg of powdered soil CRM (particle size does not exceed 80 μm) and 100 mg of spectroscopic buffer (graphite powder containing 15 wt% NaCl) were carefully mixed for 10 min to homogenize the sample. Further, the sample was sequentially diluted 5 and 10 times. In this way, 2-, 10-, and 100-fold diluted samples were obtained.

Calibration samples

Calibration samples based on graphite powder containing 15 wt% NaCl with impurity concentration range of 0.01 - 500 μg g^{-1} were used for construction of calibration curves. These samples were prepared from Russian State CRMs of graphite powder with different combinations of impurities (SOG-24, SOG-37, SOG-21 containing 24, 37, and 21 elements, respectively; Ural State Technical University).

Results and Discussion

Matrix effects

The problem of calibration samples is well known to be a key problem in analysis of solid samples. In the present study, an attempt to analyze a wide range of elements in soils by TJP-AES using calibration samples based on graphite powder was undertaken. CRMs of graphite powder with different sets of impurities are available; moreover, introducing needed element into graphite is not a difficult task. For soils having variable and complex mineral composition, this opportunity

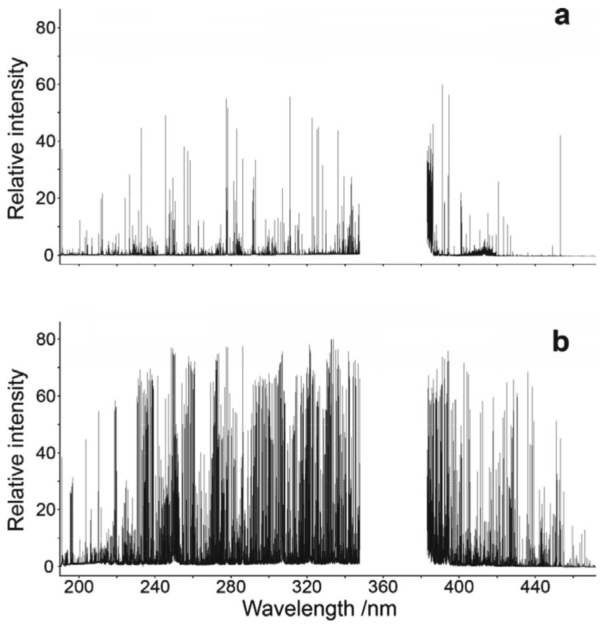

Fig. 2 Spectra: a, graphite powder containing 30 impurities; b, a 2-fold diluted SKR-3 soil.

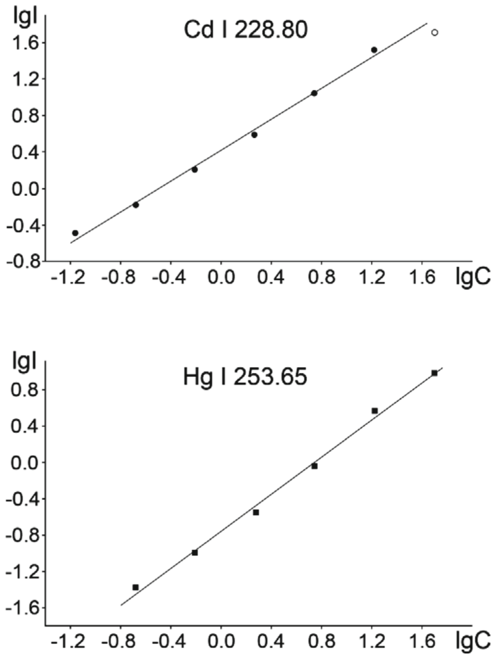

Fig. 4 Calibration curves for Cd I 228.80 and Hg I 253.65 (C/μg g^{-1}).

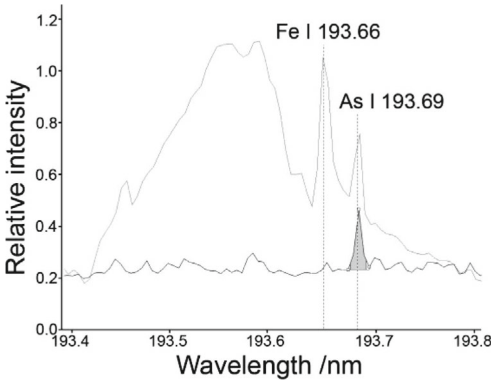

Fig. 3 As I 193.69 line obtained for graphite powder (lower graph) and a 2-fold diluted SKR-3 soil (higher graph).

seemed to be very attractive but very doubtful due to a great difference in matrix composition of analyzed and calibration samples, which can lead to different contribution of non-spectral and spectral matrix effects on analytical signal of elements (Table 2).

The soil spectra are rather complex and the pronounced spectral interferences are very likely. The spectra of graphite powder containing 30 impurities (50 μg g^{-1} of each element) and a 2-fold diluted SKR-3 sample are given in Fig. 2. It is seen that the soil spectrum is much more abundant than the graphite one. The As I 193.69 line obtained for graphite powder and a 2-fold diluted SKR-3 soil is presented in Fig. 3. As it is seen, As I 193.69 is on the slope of Fe I 193.66 line and a wide molecular band belonging to Al species in the soil spectrum while it has a smooth background in the graphite one.

The presence of easily ionizable and transition elements having many lines in spectrum can cause non-spectral matrix effects. Al with comparatively low ionization energy (5.98 eV) may increase intensities of analytical lines while such a transition element as Fe may reduce ones.[25] These effects can partially offset each other. Disturbance of local thermodynamic equilibrium in the plasma[26,27] can also result in different behavior of ionic and atomic lines of the same element in graphite and soil, which require special attention. All these effects taking place in the plasma seemed to have to considerably complicate the direct analysis of soils, and studying the behavior of specific elements was needed.

Analysis technique

Dilution of the soil samples by a spectroscopic buffer (graphite powder containing 15 wt% NaCl) may reduce matrix effects, but also result in worsening LODs of analytes. A dilution factor (DF) depends on the nature and concentration of analyte as well as the matrix composition. The optimal DF has to eliminate matrix effects on the analytical signal and provide comparatively low LODs of anthropogenic elements. The additive of NaCl into the buffer allows increasing analytical line intensities and suppressing matrix influence to some extent.[23] To estimate matrix effects on analytical line intensities, the 2-, 10-, 100-fold diluted soil CRMs were analyzed using calibration samples based on graphite powder. Cd I 228.80 and Hg I 253.65 calibration curves are presented in Fig. 4.

It was found that a 2-fold dilution by buffer is quite enough for As, B, Cd, Cu, P and V determination in all kinds of soils investigated. The satisfactory results were obtained. For SCT and SSK, comparatively good agreement of the results with the certified values was obtained for Sn under a 2-fold dilution and for Be, Co, Cr, Ga, Nb, Pb, and Zn under a 10-fold dilution (Table 3). Although the content of As in CRMs is by an order of magnitude higher than Cd, which leads to the overlapping Cd 228.80 and As 228.81 lines, ATOM software allows for isolating the Cd signal and obtaining the correct results of Cd determination at the level of several mg kg^{-1}. For SCT-1 and SSK-1 samples, only Ni showed overstated results by 1.5 times under both a 2- and a 10-fold dilution; only the 100-fold dilution provided valid results. However, there is no noticeable overstating Ni concentration for SCT-2 and SSK-3 containing

Table 3 The analysis results of SCT and SSK soils (mg kg^{-1}, 95% confidence interval, $n = 4$)

Analytical line	DL[a]	SCT-1 (black earth)		SCT-2 (black earth)		SSK-1 (grey desert soil)		SSK-3 (grey desert soil)	
		Found value	Certified value	Found value	Certified value	Found value	Certified value	Found value	Certified value
As I 193.69	2	6.7 ± 0.9	8 ± 3	20 ± 2.9	21 ± 5	13 ± 2.1	13 ± 5	58 ± 7.9	60 ± 10
B I 208.95	2	51 ± 8.1	56 ± 4	52 ± 6.8	56 ± 4	58 ± 10	63 ± 7	56 ± 11	63 ± 7
Be I 234.86	10	1.9 ± 0.4	2 ± 0.4	8.5 ± 1.1	9 ± 2	1.5 ± 0.4	2.2 ± 0.3	22 ± 3.5	26 ± 5
Cd I 228.80	2	nd[b]	0.1 ± 0.02	2.3 ± 0.4	1.8 ± 0.4	nd	0.3 ± 0.1	7.1 ± 1.5	5.5 ± 1.3
Co I 345.35	10	12 ± 1.8	9 ± 2	53 ± 7.0	46 ± 4	18 ± 2.9	12 ± 1	180 ± 37	150 ± 10
Cr II 283.56	10	81 ± 8.5	83 ± 6	84 ± 11	83 ± 6	95 ± 12	84 ± 7	87 ± 13	84 ± 7
Cu I 223.01	2	27 ± 4.0	25 ± 2	110 ± 15	110 ± 10	30 ± 2.6	34 ± 4	290 ± 30	290 ± 10
Ga I 294.36	10	13 ± 2.1	11 ± 3	14 ± 2.7	11 ± 3	16 ± 2.4	13 ± 2	16 ± 2.8	13 ± 2
Ni I 305.08	2	54 ± 8.6	32 ± 4	140 ± 27	110 ± 10	69 ± 7.4	45 ± 4	—[c]	320 ± 10
	10	46 ± 5.8		140 ± 21		68 ± 10		360 ± 70	
	100	29 ± 3.7		100 ± 13		52 ± 8.3		340 ± 45	
Nb II 316.34	10	13 ± 2.3	14 ± 3	12 ± 1.7	14 ± 3	13 ± 1.8	13 ± 2	11 ± 1.8	13 ± 2
P I 214.91	2	700 ± 130	790 ± 90	750 ± 120	790 ± 90	610 ± 120	750 ± 40	630 ± 130	750 ± 40
Pb I 283.31	10	20 ± 3.5	18 ± 1	110 ± 14	90 ± 10	20 ± 2.9	23 ± 4	320 ± 40	280 ± 60
Sn I 284.00	2	5.2 ± 1.5	3 ± 1	26 ± 3.8	20 ± 3	5.6 ± 1.1	4 ± 1	67 ± 10	60 ± 20
V II 318.77	2	72 ± 7.4	72 ± 7	68 ± 12	72 ± 7	97 ± 9.7	90 ± 10	88 ± 13	90 ± 10
Zn II 206.20	10	60 ± 3.6	56 ± 5	220 ± 35	180 ± 20	75 ± 12	70 ± 2	390 4	391 1
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a. Dilution factor. b. Not determined. c. Signal is oversaturated.

Table 4 The analysis results of SKP soil (mg kg^{-1}, 95% confidence interval, $n = 4$)

Analytical line	Dilution factor	SKR-1 (red soil)		SKR-3 (red soil)	
		Found value	Certified value	Found value	Certified value
As I 193.69	2	11 ± 1.9	10 ± 3	45 ± 5.2	50 ± 10
B I 208.95	2	64 ± 4.7	60 ± 20	58 ± 6.3	60 ± 20
Be I 234.86	10	1.6 ± 0.2	1.6 ± 0.4	21 ± 4.3	25 ± 5
Cd I 228.80	2	nd[a]	0.12 ± 0.04	5.8 ± 0.9	5 ± 2
Co I 345.35	10	28 ± 5.8	14 ± 3	190 ± 30	150 ± 20
	100	19 ± 2.3		150 ± 15	
Cr II 283.56	10	160 ± 28	180 ± 20	210 ± 25	180 ± 20
Cu I 223.01	2	54 ± 6.2	47 ± 2	340 ± 30	310 ± 10
Ga I 294.36	10	53 ± 10	15 ± 2	54 ± 9.2	15 ± 2
	100	30 ± 4.5		31 ± 3.9	
Ni I 305.08	2	91± 16	54 ± 5	—[b]	380 ± 30
	100	90 ± 11		520 ± 75	
Nb II 316.34	2	34 ± 4.1	25 ± 6	26 ± 5	25 ± 6
P I 214.91	2	480 ± 62	440 ± 40	510 ± 50	440 ± 40
Pb I 283.31	10	55 ± 6.6	23 ± 4	440 ± 45	280 ± 60
	100	34 ± 5.4		410 ± 40	
Sn I 284.00	2	11± 1.7	5 ± 1	75 ± 15	60 ± 20
V II 318.77	2	150 ± 22	180 ± 30	140 ± 20	180 ± 30
Zn II 206.20	10	88 ± 14	87 ± 3	720 ± 60	610 ± 60

a. Not determined.
b. Signal is oversaturated.

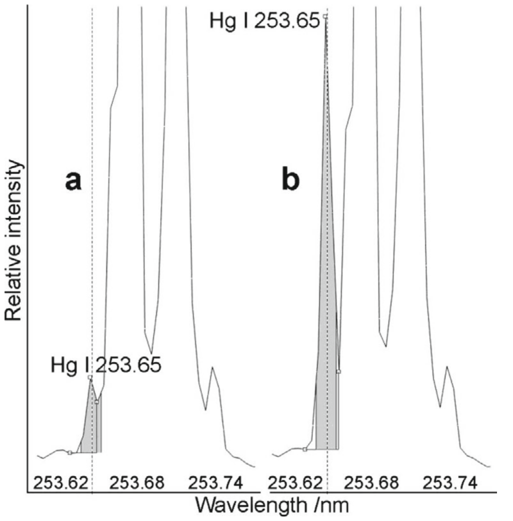

Fig. 5 Hg I 253.65 line in "Granite-10" CRMs. Concentration of Hg/mg kg^{-1}: a, 30; b, 300.

higher Ni concentrations. The lower the analyte concentration, the greater matrix effect on analytical signal takes place. Such an effect is also observed for Co I 345.35 in SSK, the increased and satisfactory results were obtained for SSK-1 and SSK-3, respectively.

More pronounced matrix effects were revealed for SKR soil containing higher concentrations of Al and Fe than SCT and SSK (Table 2). The noticeable increasing Sn concentration occurs for SKR-1, but for SKP-3 with higher Sn content, the found value satisfactorily agrees with the certified one (Table 4). In addition, the 1.5 - 2 times higher concentrations of Ga, Ni, and Pb were obtained even at a 100-fold dilution. The complexity of processes occurring in the plasma often makes it difficult to reveal the main cause of matrix influence. Overlapping Ga I 294.364 and Fe I 294.357 lines seems to result in Ga overstated concentrations.

The content of Hg is rather low in SCT, SSK, and SKR soils (0.04 - 0.4 mg kg^{-1}) and cannot be determined by the proposed direct technique (LOD of Hg in graphite is 0.3 mg kg^{-1}). However, Hg is added into the artificial "Granite-10" CRMs. The 2-fold diluted samples of "Granite-10" were analyzed using calibration samples based on graphite powder. Satisfactory results were obtained, and added and found values were in good agreement (30 and 300 are added, 32 ± 3 and 290 ± 30 mg kg^{-1} are found values, respectively). Hg I 253.652 line is situated on the slope of Fe 253.67 and Fe 253.68 lines in soil; therefore, LOD of Hg strongly depends on Fe concentration in soil. Hg I 253.652 line obtained for "Granite-10" samples is presented in Fig. 5. The technique can be applied to the analysis of soils strongly contaminated by Hg. Simple sample preparation makes it possible to minimize the probability of Hg losses.

The LODs of elements in soils provided by the technique depend on matrix composition of the samples and are the following (mg kg^{-1}): *n* for As, Be, Cd, and Sn, and $n \times 10$ for B, Cu, Co, Cr, Ga, Hg, Nb, Ni, Pb, and Zn. The relative standard deviation is in the range of 0.05 – 0.12.

In spite of some limitations caused by matrix effects, the suggested technique provides satisfactory analysis results for the majority of elements and allows for obtaining data on the element composition of soils without acid digestion of the samples.

TJP-AES is not usually used for determination of matrix elements because of self-absorption and self-reversal effects. As it is seen from Fig. 4, for Cd I 228.80, self-absorption takes place at Cd content of 50 μg g^{-1}. To determine matrix elements, multiple dilution of the sample is needed.

The considerably understated results were often obtained in the analysis of Ba, Sr, Ti and several other elements. It is most likely that these elements are well bound with Al-Si matrix, and its incomplete evaporation results in reduction of their concentration. The results presented in this work were obtained in the analytical region before the jet confluence providing better LODs of elements but worse evaporation efficiency than the region after the confluence (Fig. 1).[27,28] Using the region after the jet confluence appears to be more preferable for determination of major elements.

In this work, a small amount of 20 mg of the diluted sample was introduced into the plasma since the CRMs used are quite homogeneous. However, the method allows for introducing samples of 300 – 400 mg when heterogeneous materials are analyzed.

Conclusions

The possibility of direct analysis of soils by TJP-AES was investigated using soil CRMs of various kinds. Simple sample preparation (mixing the fine powdered soil with a spectroscopic buffer) and calibration samples based on graphite powder were used. It was shown that As, B, Cd, Cu, P, and V can be determined in all kinds of soils investigated after a 2-fold dilution of the samples by buffer. A 10-fold dilution allows for obtaining valid results of Be, Co, Cr, Ga, Nb, Pb, and Zn analysis for SSK and SCT soils, only Ni showed the noticeable increase in concentration as compared with certified values in some samples. The strongest matrix effects are revealed for SKP having the highest content of Fe and Al. For Ni, Pb and Sn, the analysis results exceeded the certified values. The overstating factor depends on analyte concentration and was no more than 2. The technique suggested allows for fast tentative assessment of a wide range of elements in soils and requires no reagents except a spectroscopic buffer.

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