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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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.

**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 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: SiO₂, 70; Al₂O₃, 17; CaO, 4; Na₂CO₃, 4; Fe₂O₃, 3; and MgO, 2 wt%.

For analysis, 100 mg of powdered soil CRM (particle size does not exceed 80 \( \mu \)m) 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 \( \mu \)g 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
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. These effects can partially offset each other. Disturbance of local thermodynamic equilibrium in the plasma 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. 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 I 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.
higher Ni concentrations. The lower the analyte concentration, the greater the 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).

The content of Hg is rather low in SCT, SKK, 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 253.65 line is situated on the challenging Mg I 208.95 line in “Granite-10” CRMs. Concentration of Hg found value satisfactorily agrees with the certified one (Table 3).

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 overestimated concentrations.

The content of Hg is rather low in SCT, SKK, 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 253.65 line is situated on the challenging Mg I 208.95 line in “Granite-10” CRMs. Concentration of Hg found value satisfactorily agrees with the certified one (Table 3).
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 × 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). 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 heterogeneous. 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 exceed the certified values. The overestimating 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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