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PROMISING OPTICAL METHODS FOR DETERMINING THE CONTENT OF HEAVY METALS IN SOILS AND SURFACE WATERS

Theoretical and hardware implementations of ion-photon spectroscopy and Doppler tomography methods to analyze the environment components with respect to the content of heavy metals (Cd, Cu, Pb, Zn) are presented. The basic quantitative characteristics determined for the methods testify to their high sensitivity to the heavy metal concentration. The method of Doppler tomography with laser excitation adapted to the problems of environmental monitoring enables the standard-free element analysis of impurities to be performed.

Keywords: ion-photon spectroscopy, laser excitation, Doppler tomography, heavy metals.

1. Introduction

Owing to the growing production and the application of heavy metals (HMs) and their high toxicity, the level of environment contamination by them is a priority indicator for ecological monitoring. The hygienically allowable contents of HMs and their compounds in components of the natural environment are rather rigid (low), which imposes high requirements on the limits of their detection and the corresponding indication methods [1].

The metrological support of ecological researches is mainly presented by well-elaborated methods and facilities such as atomic absorption (AAS) and atomic emission (AES) spectroscopies. Unfortunately, although those optical methods are selective and sensitive to the HM content (10^{-5} to $5\times10^{-6}\%$), they have a number of basic shortcomings. The main of them is a high level of systematic errors obtained in a lot of cases and originating from various matrix effects [2–4]. For their elimination, chemical modifiers, which provide a controllable chemical environment for analyzed elements at the moment of their atomization, are used most often [2]. The majority of chemical modifiers are complex compounds of palladium with organic ligands, which increases the cost of analytical control. The same is true for the application of synchrotron radiation techniques. Therefore, the development of alternative optical methods that are free from the indicated shortcomings and their implementation into the technology of ecological monitoring compose a challenging task.

From this point of view, a complex of optical methods – ion-photon spectroscopy (IPS) and Doppler tomography (DT) – developed by us for the element analysis of various substances [5–9] can be very promising. Under stationary conditions of ionic irradiation of a substance, the percentage contents of sputtered atoms in the flow do not depend on their sputtering probabilities, being determined by the initial target composition only. Therefore, both IPS and DT, as well as other secondary-emission techniques of surface diagnostics using ionic beams, are free from matrix effects [4–6].

The most informative parameters that characterize a flow of atomic particles flying away from the surface are their distribution functions over the velocities, $f_i(v_l)$. Of the methods aimed at measuring $f_i(v_l)$, the most known ones are energy- and angle-resolved secondary ion mass spectrometry, ion scattering spectroscopy, and Doppler shift spectroscopy of laser-induced fluorescence [4,6]. However, the data for $f_i(v_l)$ provided by all of them are restricted with respect to both the parameter i and the velocity. In addition, those techniques require that special fields or devices in a vicinity of the analyzed target should be applied, which restricts the scope of their practical application. Moreover, the application of the mentioned methods, as well as the others used in ecological monitoring [1–3], requires that reference (standard) specimens should be used, with the fabrication of the latter considerably slowing down the analysis procedure, complicating it, raising its cost, and, sometimes, even making it impossible. Nowadays, the probability of particle excitation owing to the interaction of particles with a surface can be determined, if no reference specimens are made use of, only by applying the method of Doppler tomography with laser excitation of secondary atoms (DTLE) [10]. Special excitation conditions enable the realization of the standard-free element analysis of materials, provided that the distribution of particles over their velocities is known. The DT technique allows this distribution to be determined directly. In the express version of DT, the distribution is taken from a databank of previously measured distributions, or it is calculated theoretically, with the error not exceeding 5–7% [9].

Hence, in order to elucidate the capabilities of IPS and DTLE, as well as the expediency of their introduction into the technology of ecological monitoring, those methods have to be adapted to the specific features of monitoring, the analytical capabilities of the methods have to be determined at the quantitative level, and a comparison with the capabilities of other existing techniques has to be made. As the objects of investigation, we selected Cd, Cu, Pb, and Zn metals. Those are dangerous HMs, the impact technogenic inflow of which into the Zakarpattya's natural landscapes, according to the results of search experiments [11], is substantial, exceeds the maximum permissible levels, and needs to be monitored.

2. Experimental Hardware and Techniques

2.1. Experimental installation

The DT and IPS techniques were implemented in the same device, a Doppler tomograph, which was described in works [6, 8] in detail. As probing particles, K^+ ions were used, which do not induce appreciable changes in the ion-photon emission (IPE) spectra [5]. The primary beam was formed in an ion source according to the surface ionization mechanism, which allowed us to obtain K^+ ions highly uniform with respect to both the particle kind and the charge multiplicity. During the experiment, we created conditions when, at insignificant bulk diffusion, such an equilibrium regime was established in the course of ionic bombardment that the composition of sputtered substance was identical to the bulk one. For this purpose, we carried out researches at an ion energy of 10 keV, a current density of 7.5–12.8 $\mu A/cm^2$ at the target surface, and a vacuum of about 10 Torr. The selected parameter values allowed us to reduce the effect of specimen surface charging by the ion beam and to avoid the secondary effects associated with the variations of both the sputtering coefficients and the emission probabilities for excited impurity atoms.

Radiation in the spectral range from 250 to 800 nm was analyzed on an MDR-6U monochromator, its filtration was carried out on a scanning Fabry–Pérot interferometer (for DT), and its registration was executed with the use of the photo-electric method. The Doppler tomograph provided the following capabilities: 1) the creation of correct experimental conditions for the measurement of differential IPE characteristics; 2) an equivalent collection efficiency for photons spontaneously emitted by excited particles at different points in space; 3) the measurement of one-dimensional distributions $f_i(v_l)$ along different spatial directions with the use of the Doppler technique; 4) the possibility of one-photon resonance excitation of emitted particles with the help of radiation generated by a continuous-wave laser based on the rhodamine 6G dye with a wide generation line (0.2 nm) that overlaps the Doppler contour of the absorption line for those particles; and 5) the uniform illumination of a plane layer h oriented in parallel to the surface with laser radiation. Unfortunately, the generation band of an available laser (570–640 nm) did not allow us to excite the sputtered impurity atoms from the ground state "0" into a definite state "i". An alternative way for today, which was realized in this work, consists in theoretical calculations of excitation probabilities for sputtering Cd, Cu, Pb, and Zn atoms taking the actual parameters of a laser beam into account.

2.2. Ion-photon spectroscopy

Let us introduce the metrological characteristics of IPS regarded as a simplified version of DTLE. The element analysis in IPS (and in DT) is usually carried out with respect to the characteristic IPE spectral lines belonging to secondary excited atoms. The quantitative analysis is known [5, 6] to be reduced to the following procedure: 1) the impurity spectral line intensity I_{ij} for the selected transition $i \to j$ is measured and used to determine the yield Y_{ij} of photons per incident ion for this transition, 2) the value of Y_{ij} is used to determine the sputtering coefficient s_i for those particles, 3) the obtained s_i-value is used to calculate the total sputtering coefficients s_d for impurity atoms, and 4) s_d is used to determine the impurity concentration C_d in the examined material according to the formula

$$C_d = s_d/S, \tag{1}$$

where S is the total (over all elements) sputtering coefficient of the material. The most complicated is the penultimate stage 3, namely, the determination of s_d from known s_i. Those quantities are coupled by the relation

$$s_i = N_i\, s_d, \tag{2}$$

where N_i is the probability of forming the i-th excited state of impurity atoms averaged over their velocities. The only way for today to find the probability N_i is the application of standard specimens. For this purpose, the quantitative content of HMs in the examined probes, i.e. their total amount and the fraction of their mobile forms, was defined with the help of an atomic-absorption spectrometer contrAA 700. Provided that the concentration C_d is known, the probability N_i can be determined, by using the relation

$$N_i = \frac{Y_{ij}}{A_{ij}}\, \tau_i\, S\, C_d, \tag{3}$$

where A_{ij} is the probability of the $i \to j$ transition per unit time, and τ_i the lifetime of the i-th state.

The most important quantitative characteristic of IPS is the threshold concentration sensitivity of the method with respect to impurities (in terms of photon/ion units),

$$H_{\mathrm{th}} = \frac{dY_{ij}}{dC_d} = A_{ij}\, \tau_i\, N_i\, S. \tag{4}$$

However, this value is not reached on available experimental installations (the same is true for any other technique). The actual sensitivity of an ion-photon spectrometer operating in the single-photon counting mode equals (in terms of pulse/ion units)

$$H = \frac{1}{4\pi}\, \eta\, K\, \Omega\, H_{\mathrm{th}}, \tag{5}$$

where η and K are the quantum yield of the photocathode in a photoelectronic multiplier and the optical transmittance of the system, respectively. The sensitivity H is responsible for another important quantitative parameter of the method, namely, the impurity detection threshold $C_{\min}$, i.e. the minimum relative concentration of impurity that can be revealed in the studied specimen with a given probability with the use of a specific ion-photon spectrometer. According to Eqs. (1), (4), and (5), we obtain

$$C_{\min} = \frac{q I_{ij}^{\min}}{H I_p}, \tag{6}$$

where q is the charge of a primary ion, $I_{ij}^{\min}$ the minimum intensity of the line (in terms of pulse/s units) required for the latter to be detected with a given probability, and I_p the current of primary ions. The impurity detection threshold was determined for the typical case $I_p = 10\ \mu$A.

2.3. Doppler tomography with laser excitation

Under certain conditions of resonant single-photon excitation with the use of a laser, each impurity atom sputtered by ions can spontaneously emit a number of photons [12]. By registering the glow emitted by impurity atoms at the transition $i \to 0$, one can measure the photon yield parameter, Y_{i0}, i.e. the average number of photons spontaneously emitted by those particles per primary ion. Taking into account that the sputtering coefficient for impurity atoms in the ground state is approximately equal to that for the impurity, s_d, its absolute value amounts to

$$s_d = Y_{i0} \frac{\displaystyle\int dv_z \frac{f_i(v_z)}{w_{i0}(v_z)}}{\displaystyle\int dv_z f_i(v_z)}. \tag{7}$$

Here, $w_{i0}(v_z)$ is the probability for a sputtered impurity atom that is in the ground state “0”, flies away from the surface, and possesses the normal to the surface component v_z of the velocity $\mathbf{v}$ to transit onto the level "i" in the field of laser radiation and to spontaneously emit a photon (integration in Eq. (7) is carried out over the whole interval of possible v_z-values); and $f_i(v_z)$ is an arbitrarily normalized distribution function of those particles over v_z, i.e.

$$f_i(v_z) = f_0(v_z)\, w_{i0}(v_z), \tag{8}$$

where $f_0(v_z)$ is the distribution of impurity atoms emitted in the ground state "0" over v_z.

Note that the ratio between the integrals in Eq. (7) has an exact physical meaning. This is the function $w_{i0}(v_z)$ [10] averaged over the particle velocities, i.e. the average number W_{i0} of photons spontaneously emitted by an impurity atom,

$$W_{i0} = \frac{\displaystyle\int dv_z f_0(v_z) w_{i0}(v_z)}{\displaystyle\int dv_z f_0(v_z)} = \frac{\displaystyle\int dv_z f_i(v_z)}{\displaystyle\int dv_z \frac{f_i(v_z)}{w_{i0}(v_z)}}. \tag{9}$$

Hence, the standard-free element analysis in the framework of the DTLE method is reduced to the first-principles calculation of the probability $w_{i0}(v_z)$ and to the measurement of the absolute photon yield Y_{i0} and either of the distributions $f_i(v_z)$ or $f_0(v_z)$ with the help of DT facilities. As follows from Eqs. (1), (7), and (9), the partial impurity concentration C_d is determined from the relation

$$C_d = \frac{Y_{i0}}{W_{i0}}\, S. \tag{10}$$

The calculation procedure for the probability of secondary atom excitation by laser radiation at the $0 \leftrightarrow i$ transition in the framework of the two-level excitation-deexcitation scheme, which is often realized in practice, was considered in works [8, 10]. The main requirement consists in that the measurement of the laser radiation characteristics should be done at every point of the volume, where the emitted particles are excited, and that the corresponding data should be introduced into the problem. The realization of this condition distinguishes DTLE from the laser-induced fluorescence [12] and, in contrast to the latter, makes the standard-free analysis possible. The final formula for the sought probability in the case where a spatial layer of the thickness h is illuminated with a laser reads

$$w_{i0}(v_z) = n_i\left[\frac{h}{\tau_i v_z} + \left(1 - \frac{1}{A}\right)\left(1 - e^{-\frac{Ah}{\tau_i v_z}}\right)\right]. \tag{11}$$

The quantities n_i and A are determined by the relations

$$n_i = \frac{g_i S_k}{g_0 A}, \tag{12}$$

$$A = 1 + S_k\left(1 + \frac{g_i}{g_0}\right). \tag{13}$$

Here, g_i and g_0 are the statistical weights of levels "i" and "0", respectively;

$$S_k = P\frac{\lambda^5}{16}\,\pi^2\hbar\, c^2\sigma \,\triangle\lambda \tag{14}$$

is the saturation parameter [12]; P is the laser radiation power; λ is the wavelength corresponding to the radiative transition $0 \to i$; σ is the area of the laser beam transverse cross-section; and $\triangle\lambda$ is the laser line width. In this work, the following values of laser parameters typical of the Doppler tomograph were used: $P = 0.3$ W, $\sigma = 10$ mm^2, and $\triangle\lambda = 0.2$ nm. Note that the quantity h is the only parameter of laser excitation which can be varied at the given laser power and which considerably affects the probability of such an excitation. In order to make an optimal choice for the thickness h, we plotted the dependence $W_{i0}(h)$ by carrying out a computer simulation of the HM excitation with the use of a laser. A criterion for such a choice was the maximum value obtained for W_{i0}. In this case, however, the h-value must be in agreement with the dimensions of both input and output monochromator slits, as well as with the entrance diaphragm diameter in the Fabry–Pérot interferometer. On the basis of those results, we selected $h = 1$ mm.

The general routines of standard-free DT analysis (the ordinary and express procedures) differ from each other only by which of distributions $f_i(v_z)$ and $f_0(v_z)$ is determined. In the framework of the ordinary procedure, the function $f_i(v_z)$ is found by directly measuring the Doppler contour of a spectral line corresponding to impurity atoms and solving the known convolution-type integral Fredholm equation of the first kind [6]. However, in this work, we used the express procedure and calculated the distribution $f_0(v_z)$. For this purpose, we used the software package of molecular dynamics programs "Graze" [13].

The quantitative characteristics of DTLE are determined almost similarly to their counterparts in the IPS method (formulas (4)–(6)). But, instead of the averaged probability N_i of natural excitation of secondary atoms, the probability W_{i0} is used. Accordingly, for the threshold concentration sensitivity of the DT method, we obtain

$$H_{\text{th}} = W_{i0}\,S \qquad (15)$$

instead of Eq. (4). For the actual concentration sensitivity H of a Doppler tomograph and the impurity detection threshold $C_{\min}$, formulas (5) and (6) remain valid.

2.4. Methods of soil and water sample preparation for the analysis

Procedures of preliminary soil and water sampling from urbanized territories (near the town of Uzhgorod) for their analysis satisfied the conventional standards [14, 15]. Samples were taken from nine areas located near highways. We developed three techniques for fabricating the targets from the collected soil and surface water specimens, which would be suitable for researches using the IPS and DT methods under ultrahigh vacuum conditions. One of them is applied before the total concentration of HMs in soils is analyzed using the indicated techniques, the second one before the content of mobile HM forms in soils is determined, and the third one precedes the determination of the HM concentration in surface waters.

In the former case, a soil sample was preliminarily subjected to the procedure of mineralization of available organic compounds in a muffle furnace. The next careful agitation of the sample provided the maximum homogeneity of the environment around HM atoms in a material and, accordingly, the reproducibility and the repeatability of the results obtained. Then, the material was pressed (under a pressure of 200 kg/cm^2) into a pellet $10 \times 10 \times 3$ mm^3 in dimensions. According to the second procedure, a soil sample intended for the determination of the contents of mobile forms of heavy metals in it using the IPS or DT method was preliminarily subjected to the known procedure of chemical extraction [2] of HMs that were available in those forms. The obtained acid extract of HMs was evaporated and mineralized to the state of solid residual used for fabricating a target. The third procedure of preparing the samples was developed for the determination of the HM concentration in surface waters. Its distinction from the previous one consisted only in that the water sample itself rather than the acid extract of HMs was made use of.

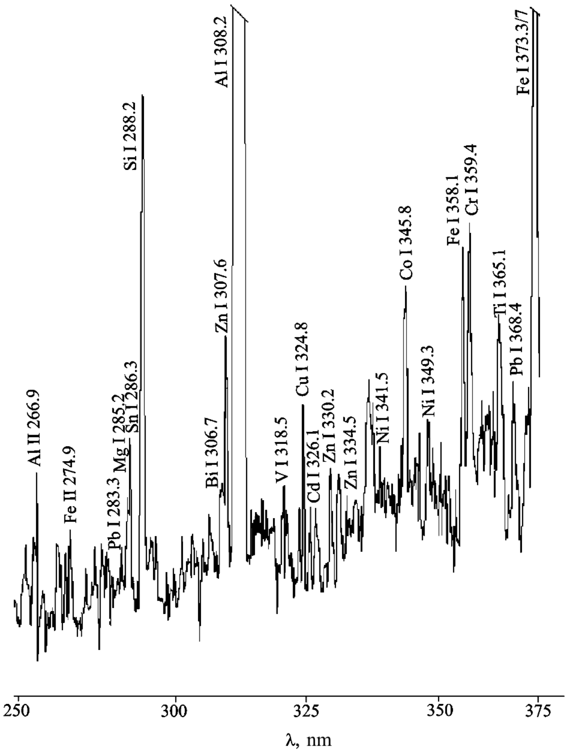

Fig. 1. Section of a IPE spectrogram for soil sample 3

3. Results and Their Analysis

The qualitative element IPS-analysis of the total HM content in the examined samples was carried out by recording and identifying the spectrograms of ion-photon emission. A typical section of the spectrogram is depicted in Fig. 1. The spectra have practically identical collections of spectral lines. However, the line intensities and, correspondingly, the component concentrations in different soil samples are considerably different. As a result, the following elements were detected: Si, Al, Mg, Fe, Cu, Pb, Zn, Sn, V, Ni, Cr, Sr, Mo, Cd, Li, Bi, Ti, Te, Ca, Ba, and Rn. In other words, the soils are characterized by complicated chemical compositions and possess, besides natural components, a significant amount of technogenic HM impurities. Among the latter, Cd, Pb, Zn, and Co, as well as radioactive Sr and Rn, are highly dangerous. The most intense are the resonance lines of

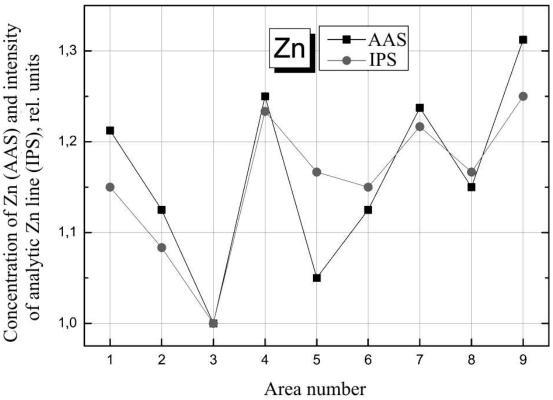

Fig. 2. Comparison of AAS and IPS methods on the basis of the data concerning the spatial nonuniformity of the total Zn concentration in soils

sputtered aluminum, copper, iron, and silicon atoms and scattered potassium ones. A substantial absolute content of indicated elements in the studied samples is natural, because one third of the soil solid phase falls on silicon, and more than 10% on aluminum and iron [16]. We should also emphasize a considerable emission by atomic magnesium (Mg I 382.9, 383.2, 517.2, and 518.4 nm) entering the composition of iron-magnesium clays (about 0.6%) in soil. The IPE spectra of all nine samples were practically the same with respect to the intensities of the lines of those elements, which testifies to an identical contribution made by the natural component to the element composition of soils over the researched territory.

The analysis of IPE spectra demonstrates a high concentration sensitivity of IPS method with respect to heavy metals. Some sections reveal Re exotic for soils (Re I 346.0 nm) and Rh (Rh I 343.4 nm), which enter as catalysts into high-octane grades of gasoline. The major factors affecting the amount of HMs in soils on the examined areas are the mechanical and physico-chemical parameters of soils and the magnitude of anthropogenic pressure [11].

Table 1. **Total concentrations C_d and photon yields Y_{ij} for soil from area 3**

Metal	Analytic line, nm	C_d, mg/kg	C_d, at.%	Y_{ij}, photon/ion
Cd	Cd I 643.9	0.65	1.2×10^{-5}	2.3×10^{-9}
Cu	Cu I 324.8	34.5	1.1×10^{-3}	2.1×10^{-7}
Pb	Pb I 368.4	32.8	3.2×10^{-4}	7.2×10^{-8}
Zn	Zn I 307.6	98.2	3.1×10^{-3}	1.2×10^{-6}

In order to disclose the analytical capabilities of IPS and compare them with the capabilities of AAS, we measured the absolute intensities of the selected spectral lines emitted by Cd, Cu, Pb, and Zn for all prepared samples. These analytical, in the IPS sense, lines (they are the most intense lines on the spectrograms and can be resolved using the system of optical radiation registration and analysis) are as follows: Cd I 643.9, Cu I 324.8, Pb I 368.4, and Zn I 307.6 nm; with the lines Cu I 324.8 and Zn I 307.6 nm being the resonance ones.

The determination of the absolute intensities makes it possible to directly compare the AAS and IPS methods, in particular, using the data obtained for the spatial nonuniformity of the total HM concentration in soils. This comparison for Zn is illustrated in Fig. 2. For convenience, the HM concentrations determined from the AAS data and the intensities of corresponding analytical IPS lines were plotted in relative units (normalized to the corresponding values for area 3). As is seen from Fig. 2, the AAS and IPS data obtained for the spatial distribution of the total HM concentration do not coincide absolutely, even making allowance for the measurement errors. However, such a coincidence should not take place, at least owing to the difference between the mechanisms of useful signal formation in those methods. The different AAS and IPS mechanisms result in the different manifestations of changes in the HM atom environment when changing from one examined area to another. Owing to the absence of matrix effects, the IPS should expectedly demonstrate a weaker influence on the useful signal and, accordingly, a better proportionality between the latter and the HM concentration. From Fig. 2, one can see that we obtain a good correlation between the AAS and IPS results rather than their complete coincidence. In particular, the Pearson correlation coefficient for Zn amounts to 0.835 at a significance level of 5.05×10^{-3}. Similar close correlations between the AAS and IPS data were also obtained for Cd, Cu, and Pb, as well as for the mobile forms of HMs in soils and for their contents in surface waters.

While determining H_{th}, H, and $C_{\min}$ in the framework of the quantitative element IPS analysis of soils with respect to the total content of Cd, Cu, Pb, and Zn metals, we used the research results – i.e. the total concentrations of the indicated HMs determined by the AAS method and the absolute intensities I_{ij} of

Table 2. **Excitation probabilities N_i and parameters $H_{\rm th}$, H, and $C_{\rm min}$ in the case of quantitative element IPS analysis of soils with respect to the total contents of Cd, Cu, Pb, and Zn heavy metals**

Analytic line, nm	N_i	$H_{\rm th}$, photon/ion	H, pulse/ion	$C_{\rm min}$, at.%	$C_{\rm min}$, mg/kg
Cd I 643.9	6.8×10^{-3}	2.7×10^{-2}	2.3×10^{-5}	6.9×10^{-7}	3.8×10^{-2}
Cu I 324.8	4.7×10^{-3}	1.9×10^{-2}	1.6×10^{-5}	1.0×10^{-6}	3.1×10^{-2}
Pb I 368.4	5.5×10^{-3}	2.2×10^{-2}	1.9×10^{-5}	8.5×10^{-7}	8.5×10^{-2}
Zn I 307.6	9.7×10^{-3}	3.9×10^{-2}	3.3×10^{-5}	4.8×10^{-7}	1.5×10^{-2}

Table 3. **Probabilities W_{i0} and parameters $H_{\rm th}$, H, and $C_{\rm min}$ in the case of quantitative standard-free element DT analysis of soils with respect to the total HM content**

Analytic line, nm	W_{i0}, photon/atom	$H_{\rm th}$, photon/ion	H, pulse/ion	$C_{\rm min}$, at.%	$C_{\rm min}$, mg/kg
Cd I 326.1	1.2×10^{-1}	4.8×10^{-1}	4.1×10^{-4}	3.9×10^{-8}	2.1×10^{-3}
Cu I 324.8	2.6×10^{-1}	1.0	8.9×10^{-4}	1.8×10^{-8}	5.6×10^{-4}
Pb I 283.3	2.1×10^{-1}	8.4×10^{-1}	7.2×10^{-4}	2.2×10^{-8}	2.3×10^{-3}
Zn I 307.6	1.9×10^{-1}	7.6×10^{-1}	6.5×10^{-4}	2.5×10^{-8}	7.8×10^{-4}

their analytical lines measured by the IPS method – obtained for samples from area 3 (with the lowest HM content) as the input data. The calculated concentrations C_d and the photon yields Y_{ij} determined from I_{ij} are quoted in Table 1.

It is important that, using the AAS method, the concentrations were determined in terms of mg/kg units, but formulas (1), (3), and (4) include relative concentrations (in terms of impurity atom per matrix atom units). Therefore, the C_d-values were recalculated into the relative concentrations. The corresponding results multiplied by 100 are also quoted in Table 1. While recalculating the concentration from the mg/kg units into the impurity atom/matrix atom ones, we used the following typical element composition of soil [16]: O – 49%, Si – 33%, Al – 7.13%, Fe – 3.80%, C – 2.0%, Ca – 1.37%, K – 1.36%, Na – 0.63%, Mg – 0.63%, N – 0.1%, and so on.

According to the data presented in Table 1 and formula (3) and using the total (over all elements) sputtering coefficient S found in the IPS experiments for the studied soil sample from area 3, $S = 4.03$ atom/ion, we determined the probabilities N_i and, then, the values of the parameters $H_{\rm th}$, H, and $C_{\rm min}$. To calculate H, we took $\eta = 0.1$ pulse/photon and $K = 0.5$ (those values are quite feasible for the modern detectors of optical radiation and monochromators with high-efficient diffraction gratings). The results obtained are quoted in Table 2.

The probabilities N_i and the parameters $H_{\rm th}$, H, and $C_{\rm min}$ in two other cases, namely, the analysis of soils with respect to the content of mobile forms of Cd, Cu, Pb, and Zn and the analysis of surface waters with respect to the content of the same heavy metals, were calculated analogously. At the quantitative level, the data obtained characterize the analytical capabilities of the IPS method concerning the determination of the HM content in soils and surface waters. In particular, they testify to a high sensitivity of the method; namely, the threshold of HM detection amounts to 10^{-7}–10^{-6} at.% for all samples under investigation. While comparing the $C_{\rm min}$-values obtained by us with the detection thresholds for HM concentrations in soils typical of the most widespread techniques, it follows that, by its sensitivity, IPS prevails over the modern analytical methods for ecological monitoring [1, 3, 4]. This fact is a consequence of the high excitation probabilities for secondary HM atoms. The values of N_i fall within the interval from 10^{-4} to 10^{-2} for all analyzed samples of soils and surface waters. These are very large values for the ion-photon emission phenomenon [5–7, 17], which may probably be associated with the well-known “chemical” effect in IPE [5], namely, a substantial increase of the excitation probability for secondary atoms owing to the presence of oxygen in targets in a sufficient amount (SiO_2 is the basic component of material in all examined samples).

At last, it should be noted that the parameters $H_{\rm th}$, H, and $C_{\rm min}$ of the method do not vary considerably when changing from the analysis of soils with respect to the total HM content to their analysis with respect to the content of mobile forms of metals and, further, to the analysis of surface waters with respect to the HM content. This circumstance is evidently associated with the fact that the environment of HM atoms in the examined samples and the velocity distributions of sputtered particles change weakly. Accordingly, the probabilities of the natural excitation of secondary atoms and the corresponding values averaged over the velocities, i.e. the probabilities N_i, do not change substantially, which means that it is also true for the parameters $H_{\rm th}$, H, and $C_{\rm min}$.

To adapt the DTLE method and make it suitable to detect HMs in the environment components, the choice of analytical spectral lines is very important. According to formula (11), only two parameters of spectral lines considerably affect the probability of the laser excitation of secondary atoms; these are the wavelength λ and the lifetime τ_i of the upper level in a spectral transition. Therefore, the choice of lines was based on the dependences $W_{i0}(\lambda)$ and $W_{i0}(\tau_i)$ [8]. The method should be better implemented, by using those lines that correspond to the most long-wave transitions with the shortest lifetimes of excited states (they are indicated in the parentheses): Cd I 326.1 (2.7×10^{-8} s), Cu I 324.8 (0.98×10^{-8} s), Pb I 283.3 (1.7×10^{-8} s), and Zn I 307.6 (1.3×10^{-8} s). So, one can see that the DT and IPS methods can differ from each other by analytical lines.

The probabilities W_{i0} and the parameters $H_{\rm th}$, H, and $C_{\rm min}$ calculated with the use of the express technique for the selected lines in the framework of quantitative standard-free element DT analysis of soils with respect to the total HM content are presented in Table 3. By comparing the data in Tables 2 and 3, one can see that the probability W_{i0} of the laser excitation of impurity atoms in the DT method is more than an order of magnitude (usually, two orders of magnitude) higher than the probability N_i of the natural excitation of particles in the IPS method. Accordingly, the parameters $H_{\rm th}$, H, and $C_{\rm min}$ in the case of Doppler tomography are quantitatively better than those of ion-photon spectroscopy by the same factor. Moreover, as was shown above, the IPS method itself is characterized by a high sensitivity to HMs. Hence, for the available hardware facilities, the concentration sensitivity of the proposed technique is not worse than that of the diagnostic method [18] based on the ionization of secondary particles by laser radiation and considered to be the most sensitive. It should also be noted that DT is capable of increasing W_{i0} further by approximately two orders of magnitude owing to the growth of the laser radiation power from 0.3 to 10 W. However, the largest advantage of DT is the possibility of standard-free analysis, which makes its duration time considerably shorter.

In the framework of the DT method, the difference between the cases where soils are analyzed with respect to the total HM content, or they are analyzed with respect to the content of mobile forms of metals, or surface waters are analyzed becomes even more smaller, because the probabilities $w_{i0}(v_z)$ of the laser excitation do not change in all those cases, in contrast to the probabilities of the natural excitation of particles in the IPS method. In principle, only the velocity distributions $f_i(v_z)$ (or $f_0(v_z)$) can be different in different cases. However, the slight differences in details of those distributions cannot considerably affect the result of averaging $w_{i0}(v_z)$ over the velocities v_z, i.e. the value of W_{i0}. The latter quantity has a key character and governs the parameters $H_{\rm th}$, H, and $C_{\rm min}$. Table 3 illustrates the analytical capabilities of DT in all three cases.

4. Conclusions

In order to adapt the IPS and DT methods to ecological monitoring problems, the procedures of producing samples-targets were developed, which could be applied in the framework of those methods to determine the total content of HMs and the content of mobile HM forms in soils, as well as the concentration of HMs in surface waters. The corresponding analytical lines were determined separately for IPS and DT, and the optimal conditions for the secondary HM atom excitation by laser radiation in a Doppler tomograph were found.

If the ecological monitoring problems of determining the qualitative composition of soils and surface waters and detecting the most toxic components in them – these are heavy metals, in particular, Cd, Cu, Pb, and Zn – are to be solved, the qualitative IPS analysis turns out one of the most effective and cheap express methods of researches. Its advantages consist in a high accuracy of the element identification typical of optical techniques (moreover, a number of elements can be identified in the same experiment) and in that information can be registered at some distance from the examined area.

The role of IPS and DT in obtaining the primary data for ecological monitoring is determined by the basic quantitative characteristics found for those methods (such as the threshold concentration sensitivity, the concentration sensitivities of available experimental realizations of the methods, and the impurity detection threshold) for the cases of soil analysis with respect to the total content and the content of mobile forms of Cd, Cu, Pb, and Zn, as well as the analysis of surface waters with respect to the content of the indicated elements in them. In all cases, the methods were found to be highly sensitive to heavy metals. In particular, the impurity detection threshold for various HMs by the IPS method amounted to 10^{-7}–10^{-6} at.%, whereas the sensitivity of the DT method turned out to be almost two orders of magnitude higher. Moreover, the sensitivity of the latter method can be further enhanced by increasing the radiation power of the laser in a Doppler tomograph. The IPS and DT methods prevail over the modern optical ones – atomic absorption and atomic emission spectroscopies – not only in their sensitivity to HMs, but also in the analysis accuracy, because such a powerful source of errors as the matrix effects is excluded from them. The version of the DT method with laser excitation possesses even a more considerable advantage: it makes possible the standard-free element analysis of soil and water with respect to the HM content. In addition, there is no necessity in the creation of the bank of standard samples. In the framework of the indicated analysis, the IPS and DT methods can be used as follows. The former is applied to carry out the high-sensitive qualitative element analysis of a sample with respect to the HM content. Afterwards, with the use of the DT method, the superhigh-sensitive standard-free element analysis is performed to determine the concentration of every element found in the sample.

1. S.A. Balyuk, A.I. Fateev, and M.M. Miroshnychenko, *Geochemical Soil Inspection at Urbanized Terrains. Methodical Recommendations* (Sokolovskyi Inst. of Soil Sci. and Agricult. Chem., Kharkiv, 2004) (in Ukrainian).
2. D.L. Kotova, T.A. Devyatova, T.A. Krysanova, N.K. Babenko, and V.A. Krysanov, *Methods of Soil Quality Monitoring* (Voronezh State Univ., Voronezh, 2007) (in Russian).
3. M.C. Brennan, *A Practical Approach to Quantitative Metal Analysis of Organic Matrices* (Wiley, Wiltshire, 2008).
4. R.J.C. Brown and M.J.T. Milton, Trends Anal. Chem. **24**, 266 (2005).
5. S.S. Pop, S.F. Belykh, V.G. Drobnich, and V.Kh. Ferleger, *Ion-Photon Emission of Metals* (FAN, Tashkent, 1989) (in Russian).
6. V.G. Drobnich, S.S. Pop, and V.A. Esaulov, *Doppler Tomography of Surface-Emitted Particles* (Zakarpattya, Uzhgorod,1988) (in Russian).
7. S.S. Pop and I.S. Sharodi, Izv. RAN Ser. Fiz. **68**, No. 2, 277 (2004).
8. V.G. Drobnich, S.V. Okhrimenko, S.S. Pop, I.S. Sharodi, and O.M. Konoplyov, Ukr. Fiz. Zh. **48**, 186 (2003).
9. V.G. Drobnich, Izv. Ross. Akad. Nauk. Ser. Fiz. **62**, 1382 (1998).
10. V.G. Drobnich, S.V. Okhrimenko, S.S. Pop, amd I.S. Sharodi, Patent No. 42395A, Ukraine, MKI G01N23/00 (Promysl. Vlasn. Ofits. Bul. N 9, 2001).
11. I.S. Sharodi, I.E. Mytropolsky, M.V. Prykhod'ko, V.S. Buksar, M.I. Lingur, L.M. Markovych, and S.S. Pop, Visn. Kharkiv. Univ. **34**, 239 (2011).
12. H.L. Bay, Nucl. Instrum. Methods B **18**, 430 (1987).
13. V.G. Drobnich, S.V. Okhrimenko, and G.Yu. Podgoretskaya, Poverkhnost Rentgen. Sinkhrotron. Neitron. Issled. **7**, 40 (2006).
14. *State Standard of Ukraine 4287-2004. Soil Quality. Test Quality* (Derzhspozhyvkontrol Ukrainy, Kyiv, 2005) (in Ukrainian).
15. *State Standard of USSR 17.1.5.05-85. Nature Protection. Hydrosphere. General Requirements for Surface and Sea Waters, Ice and Atmospheric Precipitation Sampling* (State Committee for Standards of the USSR, Moscow, 1986) (in Russian).
16. P.M. Smirnov and E.A. Muravin, *Agricultural Chemistry* (Kolos, Moscow, 1984) (in Russian).
17. N.V. Pleshivtsev and A.I. Bazhin, *Physics of the Ion Beam Action upon Materials* (Vuzovskaya Kniga, Moscow, 1998) (in Russian).
18. P. Homolka, W. Husinsky, G. Nicolussi, G. Betz, and X. Li, Phys. Rev. B. **51**, 4665 (1995).

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ПЕРСПЕКТИВНІ ОПТИЧНІ МЕТОДИ ЩОДО ВИЗНАЧЕННЯ ВМІСТУ ВАЖКИХ МЕТАЛІВ У ҐРУНТАХ І ПОВЕРХНЕВИХ ВОДАХ

Резюме

Надано теоретичну і апаратурну реалізацію методів іон-фотонної спектроскопії та допплерівської томографії для здійснення аналізу складових навколишнього середовища на вміст важких металів (Cd, Cu, Pb, Zn). Визначено основні кількісні характеристики методів, які вказують на їх високу концентраційну чутливість до важких металів. Адаптований до задач екологічного моніторингу метод допплерівської томографії з лазерним збудженням відкриває можливість безеталонного елементного аналізу мікродомішок.