Crucible Atomizers Open Up New Opportunities for the Atomic Absorption Analysis of Trace Elements in Solid Samples with the Use of Fractional Evaporation

V. N. Oreshkin^{*a*} and G. I. Tsisin^{*b*, *c*, *}

^a Pushchino Research Center for Biological Studies, Institute of Basic Biological Problems, Russian Academy of Sciences, Pushchino, Moscow Region, 142290 Russia

^bDepartment of Analytical Chemistry, Moscow State University, Moscow, 119991 Russia ^cKurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia *e-mail: tsisin@analyt.chem.msu.ru

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Abstract—The atomic absorption analysis of trace elements in natural solid samples with the use of an improved crucible atomizer with several condensation/evaporation zones is shown to be advantageous. A new approach to fractional preconcentration is proposed, including two stages of thermal decomposition (high-temperature and low-temperature) of solid sample components when elements are evaporated and their vapors are condensed in heated and unheated zones. This approach facilitates the efficient suppression of non-selective interferences and matrix effects. It also improves the metrological characteristics of the element analysis of samples of complex composition.

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Electrochemical atomic absorption (AA) spectrometry is commonly used to determine ultralow amounts of rare and dissipated elements, such as Ag, Cd, Hg, Pb, and Tl, in environmental objects or in geological-geochemical samples. A variety of methods for the analysis of the solution, as well as methods for the direct analysis of solid samples and concentrates without chemical pretreatment, were established. This approach has always been attractive for researchers in the fields of chemical analysis and geochemistry because it simplifies the entire procedure. Moreover, it makes the occurrence of unmanageable losses of the analytes and contamination by casual impurities less likely. A variety of procedures are used to decrease non-selective interferences and matrix effects in an atomizer's analytical zone [1-3]. One of the most efficient procedures involves the preliminary fractional evaporation of solid samples with the subsequent independent atomization of the condensates. This method of selective fractional separation/concentration of volatile and moderately volatile elements, which was suggested a long time ago in atomic emission (AE) spectrometry [4, 5], is also popular in AA analysis [6-16]. In this case, atomizers are modified by designing a special condensation zone (surface) of the element vapors.

Sufficiently simple systems were developed to perform AE and AA analyses. One of them consists of a unit joining an evaporator of a solid sample and a condensate receiver with vertical zones of evaporation and condensation. These zones are functional based on a graphite crucible which has transverse heating and is designated for the analysis of 10 to 30 mg or greater amounts of solid samples [5, 6, 12, 15, 17]. The crucible construction is unchanged in these systems. The condensation zone is usually located over the crucible (heated to more than 1500°C) on the surface of a graphite rod or cylinder that is placed closely. If the sample weight, temperature, or time of fractional evaporation increase, the problems depending on the effects of base vapors, heating a condensation surface. and possible losses of the elements in question also grow. Another approach is used to determine Ag, Cd, Pb, and Tl in water concentrates, river and marine suspensions, and bottom sediments [15]. For this purpose, a crucible evaporator with two vertical condensation zones was developed. One zone heated to 700-1000°C is located in a cylinder and another unheated zone is on a rod surface located over the cylinder but not over the crucible (crucible/cylinder/rod system). After the fractional evaporation of a solid sample is finished, two condensates are analyzed in a threechamber graphite atomizer (cylinder/cell/rod) with two evaporation zones and a common isothermal analytical zone located in the cell [15]. The idea of the intermediate heated condensation zone located in the cylinder, whose temperature is significantly lower than that of the crucible/sample pair, makes it possible to raise the evaporation temperature, which is the atomization temperature of the sample in the crucible. Moreover, interferences in the analytical zone and element losses are decreased, and, conversely, the sample weight is increased.

However, this method is not always relevant for analytical problems. The fractional evaporation of solid samples, especially organomineral samples, is characterized by the intense evolution of gas-like products, emission of particles, and the formation of aerosols and their condensation on the surface of the cylinder and rod. Interferences in the analytical zone become more numerous and the metrological characteristics of the analyses become worse. This approach could be developed further as follows. For example, if a crucible atomizer/evaporator is equipped with another condensation zone, the thermal decomposition of the samples with the evaporation of the elements and condensation of their vapors could be continued in the heated and unheated zones.

In this study, we estimate the possible application of the improved crucible vaporizer with the condensation zones for the analysis of trace elements in solid samples.

MATERIALS AND METHODS

Equipment. An AA Saturn-2 spectrophotometer and a multichannel AA/AF device based on a polychromator with a deuterium background corrector were used in this study [10, 12, 15]. These instruments were equipped with atomization blocks and represented a modification of the basic model described in [10]. The models in question had several pairs of cooled graphite holders/electric contacts between which the graphite blocks of an atomizer/vaporizer-a crucible with the sample, cylinders, and a rod-were fastened. The distance between the blocks was kept within 0.5-2.0 mm. The system consisted of the vaporizer of solid samples and the receiver of condensates was thus constructed. This system was designated for the thermal decomposition and fractional evaporation of solid samples with the subsequent condensation of element vapors. After a cycle of fractional evaporation was finished, another microblock consisting of a graphite cell with a translucent analytical zone and its own holders (electric contacts) was closely adjusted without any gap between the second cylinder and the rod. The design of the three-chamber atomizer (cylinder/cell/rod) was similar to that used in [15]. This atomizer allows the simultaneous analysis of two condensates with the evaporation of elements in the common isothermal analytical zone located in the cell. Crucibles of 7 to 12 mm in height and an inner diameter of 3 to 5 mm were used for the experiments. The cylinder's height was ≤8 mm and its inner diameter was 4.5-6.5 mm. The translucent analytical zone in the cell was 2.5-4.0 mm in diameter. All the graphite blocks were preliminarily annealed at ~2100°C to remove contaminative impurities. Lamps with hollow cathodes (LSP-1,2) and electrodeless high-frequency ball lamps (VSB-2) were used as an irradiation source.

Sample preparation. Samples from different waters, suspensions, bottom sediments, and soils were analyzed. These samples originated from an area of the Prioksko-Terrasny Nature Reserve (a flood plain of the Oka River) [18]. Portions of a membrane filter with a suspension or a suspension powder (up to 30-50 mg) from bottom sediments or soils (usually diluted with graphite powder in the ratio of 1:1 or 1:5) were placed in the crucible vaporizer. To prepare reference samples solutions of the elements were added to the natural samples and to a graphite powder. Moreover, the natural samples were mixed with graphite powders which contained the known compositions of the elements. To analyze elements in river waters unfiltered $(El_{dis} + E_{sus})$ or filtered (El_{dis}) samples had to be concentrated on a DETATA sorbent under static or dynamic conditions as described in [15, 18]. Premeasured amounts of DETATA concentrates, reference samples, and control (blank) samples were placed in the crucible vaporizer. Dynamic concentration was performed on a crucible microcolumn, which also was used as a vaporizer in the cycle of fractional evaporation.

Analysis of elements in solid samples and concentrates. The cycle of the fractional evaporation of matrices in the crucible was carried out at a temperature that was gradually raised to $1700-1900^{\circ}C(10-30 s)$. The temperature of the cylinder located over the crucible was increased with a short delay to 1000°C (the first condensation zone). At the second stage of the cycle, the temperature of this cylinder was gradually raised to $1700-1900^{\circ}C$ (5-10 s), while the temperature of the second cylinder was increased to 1000°C. The condensates were analyzed in the cylinder/cell/rod atomizer with the common isothermal zone located in the cell [15, 17]. The temperature of atomization constituted 1800–2100°C (3–8 s). The crucible and the first cylinder were heated at the second stage of fractional evaporation and at the atomization stage, respectively. Two ways of signal recordingintegral and pulse recording at the wave lengths of 328.1 nm (Ag), 228.8 nm (Cd), and 276.8 nm (Tl)were used in this study.

RESULTS AND DISCUSSION

The results of this study showed that our approach based on the crucible atomizer/vaporizer is promising. The crucible/cylinder/rod system can be provided with an additional block, the graphite cylinder, which suggests the use of the block-modular principle in the construction of atomizers [17]. Thus, two consecutive stages of the high-temperature and low-temperature



Fig. 1. Atomizer/vaporizer with graphite multichamber crucible. Device is designated for thermal decomposition of solid samples and fractional evaporation/condensation of element vapors. Graphite crucible (vaporizer) (1); solid sample (2); graphite cylinders (receivers/vaporizers) (3, 4); condensate (5); graphite rod (receiver) (6); graphite cell with analytical zone placed at stage of condensate atomization (7); analytical zone (8); and replaceable cooled holders of electrocontacts (9).

decomposition of the sample components with the condensation of vapors in heated and unheated zones are possible. The improved modular vaporizer/receiver system remains sufficiently simple (Fig. 1).

The procedure of the thermal decomposition and fractional evaporation of the initial sample has one

cycle with two stages (Fig. 2). The crucible with a sample is heated at the first stage, which is high-temperature fractional evaporation. The zone of condensation/evaporation in the cylinder located over the crucible, which is low-temperature fractional evaporation, is also heated. At the second stage, the first condensation zone located in the cylinder becomes a vaporizer at >1500°C. At this stage, the condensation/evaporation zone located on the surface of the second cylinder is also heated, albeit, only to 1000°C. The condensation zone on the rod's surface is the only one which remains unheated. It should be noted that this approach was possible due to the previously developed atomizer, which had two evaporation zones and a common isothermal analytical zone designated for the simultaneous analysis of two matrices [15, 17].

The results of the analysis of the marine bottom sediment are shown in Table 1. This sample is characterized by intense matrix evaporation since it contains biogenic, chemogenic-hydrogenic, and lithogenic components. The sample was analyzed several times for the purpose of finding ways to reduce the matrix composition effect in the cycle of the preliminary transformation of the solid components [15]. The use of two stages of fractional evaporation (high-temperature and low-temperature) of the sample components leads to a higher ratio of two absorption signals: element absorption/non-selective absorption. Figure 3 demonstrates the thallium signals when analyzing a complex concentrate from river water (DETATA sorbent + suspension). This analysis was successful only in the case of preliminary fractional evaporation. However, even though one stage of fractional evaporation was used in the crucible/cylinder/rod system [15], the thallium signal was too low to separate it from that of non-selective absorption. The cycle of fractional



Fig. 2. Diagram of atomization procedure: thermal modification of solid samples and fractional evaporation/condensation of elements in crucible atomizer.

Element	No fractional evaporation stage	Single fractional evaporation stage	Two fractional evaporation stages
Ag	0.09	0.42	1.23
Cd	0.21	0.53	1.75
Tl	0.06	_	0.64

Table 1. Ratios of element absorption/non-selective absorption obtained by analysis of solid sample from bottom sediment

evaporation included in the represented atomizer model allows separating the analytical signals from interferences. Therefore, it makes it possible to determine the total amount of dissolved and suspended elements in the river water. All this is also true in the case of other environmental samples.

Some of the results of element analysis in river water, suspensions, bottom sediments, and soils are represented in Table 2. A variety of methods were used to obtain these results and support the reliability of the analysis. Moreover, the international standard of the mountain rock G-2 (granite) diluted with a graphite powder in ratios of 1:1 and 1:5 was analyzed, as previously, in this study. These mixtures were stored as 150-200 g aliquots for a long time in sealed teflon capsules and rigorously shaken prior to the analysis. The mineral composition of the standard is only partly similar to the composition of the samples studied (suspensions, bottom sediments, and soils). However, the G-2 standard belongs to the few rocks whose contents of Ag, Cd, and Tl were evaluated [19]. The fact that fractional evaporation significantly reduces the effect of the matrix composition was also considered. Analvsis was also carried out with the preliminary sample decomposition and dynamic concentration of elements from solutions (Table 2). Elements were concentrated in a crucible microcolumn filled with the DETATA sorbent and homogeneous concentrate matrices were directly analyzed [18]. Based on these data, we can conclude that this element analysis excludes significant systematic errors.

The suggested approach can thus be easily used provided that the block-modular principle is considered for the construction of crucible atomizers with vertical zones of evaporation, condensation, and atomization. Our results demonstrated that the new way of fractional evaporation allows achieving higher atomization of the mineral and organic phases of the solid samples. Also, this leads to the reduction of interferences in the analytical zone and to the stronger effect of analite separation/concentration. The relative range of element detection in solid samples characterized by significant non-selective absorption and the matrix effect is narrowed to $0.3-1.0 \times 10^{-6}\%$ for Ag and Cd. These values for Tl constitute 0.1–0.5 \times 10^{-5} %. The detection range thus is 2- to 5-fold narrower compared with the crucible/cylinder/rod system [15]. Far from the detection limit, the relative standard deviation usually did not exceed 0.20. It should also be noted that the customized test models of atomizers were used in this study.

In conclusion we would like to note that the choice of an appropriate way of fractional evaporation for



Fig. 3. Signals of thallium determination in concentrate of river water (DETATA-sorbent+suspension). Letters designate single stage of high-temperature and low-temperature fractional evaporation [15] (a); same with 0.5 μ g/g element addition (b); two stages of high-temperature and low-temperature fractional evaporation (this study) (c); and same with addition of $0.5 \,\mu$ g/g element (d).

Element	River water, μg/L		River suspension, µg/g		Bottom sediment, µg/g		Alluvial soil, μg/g		Standard G-2 (granite), μg/g		
	applied	this study	applied	this study	AA method [18]	this study	AA method [18]	this study	AA method [18]	this study	review [19]
Ag	0	0.011 ± 0.004	0	0.060 ± 0.010	0.053	0.090 ± 0.010	0.11	0.074 ± 0.08	0.083	0.032	0.040
	0.1	0.11 ± 0.03	0.1	0.15 ± 0.02						(0.034)	
Cd	0	0.018 ± 0.005	0	0.18 ± 0.03	0.14	0.23 ± 0.06	_	0.13 ± 0.03	0.11	0.027	0.016
	0.1	0.13 ± 0.02	0.5	0.66 ± 0.07						(0.022)	
Tl	0	0.004 ± 0.001	0	0.39 ± 0.08	0.45	1.1 ± 0.2	1.0+	0.55 ± 0.05	0.59	1.1	0.91
	0.1	0.09 ± 0.02	0.5	1.0 ± 0.2						(1.1)	

Table 2. Analysis of elements in natural objects (area of Pryoksko-Terrasny Reserve, Oka)

The reference samples based on mixtures of the bottom sediments and the graphite powder (1:1), as well as the graphite powder alone (values shown in brackets), were used to determine the elements in the G-2 geochemical standard.

samples with high contents of organics is promising in element analysis. This especially concerns river and marine suspensions and higher soil layers, which can include more than 50% of organic substances. This approach is based on a broad choice of the modes of thermal decomposition and combustion of volatile organoelement compounds at two stages of high-temperature and low-temperature fractional evaporation.

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