=== **SHORT COMMUNICATIONS** ===

Specialized Methods of Thermal Treatment of Riverine and Marine Suspensions Preparatorily to Their Analysis for Trace Concentrations of Chemical Elements

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Abstract—The paper considerations of the possibility of the low-temperature (1000°C) and high-temperature (>1500°C) thermal decomposition of solid samples of suspensions and the selective fractional evaporation−condensation of elements in specialized electrothermal crucible and rod atomizers for the purposes of direct atomic-absorption analysis. The approach is applied to analyze samples of riverine and marine suspensions for Ag, Cd, and Tl.

INTRODUCTION

To solve various problems of geochemistry and ecological geochemistry, it is important to know the trace-element composition of riverine and marine suspensions. Suspensions can play a leading role in the migration of trace elements with riverine waters (Gordeev, 2012; Savenko, 2006), but information on the abundances of certain minor and trace elements (Ag, Bi, Cd, Hg, Tl, etc.) in this constituent of natural waters is still scarce. Suspensions are usually separated by means of membrane filtration immediately after sampling. Analysis of minor amounts (often less than 1−5 mg) of particulate matter on membrane filters for elements is a challenging problem even when using modern and widely applied analytical techniques characterized by low detection limits, such as electrothermal atomic absorption and atomic fluorescence spectrometry (ETAAS and ETAFS, respectively), inductively coupled plasma−atomic emission spectrometry (ICP-AES), and inductively coupled plasma−mass spectrometry (ICP-MS). The reason for this is that the analytical technique employed to analyze 1 mg of a material for an element whose concentration in this material is at the level of $10^{-6}\%$ (0.01 ppm) should be able to detect 1 pg of the element, which is far from always possible. Moreover, most of the ana-lytical techniques deal with solutions, i.e., the solid material is dissolved, and the original concentration is thus even more diluted. The preparation procedure of material samples for analysis is even more complicated if microamounts of such materials should be analyzed: the routine involves preparatory concentrating (the solid are then dissolved or the elements are desorbed) (Zolotov et al., 2008). It is known that such preparatory procedures can notably affect the quality of the analytical results because of the risks of contamination or losses of the elements (chemical reactants and vessels, tools, environment and conditions in the laboratory room, etc.) (Zolotov et al., 2008; Karpov and Savostin, 2003). The effects of sample preparation procedures seem to be underestimated in geochemical research and are sometimes not identified before the researcher starts to interpret the analyses (Gordeeev, 2012; Gordeev and Oreshkin, 1990). An alternative approach is currently developed in ETAAS techniques. Prespecified portions of solid samples or concentrates are loaded into atomizers to exclude the procedure of decomposition and simplify the sample-preparation routine (Pupyshev, 2009; Oreshkin et al., 1994; Kubrakova et al., 1994). The "pure" (i.e., without modifying reactants) preparation of the suspensions or concentrates involves their thermal treatment
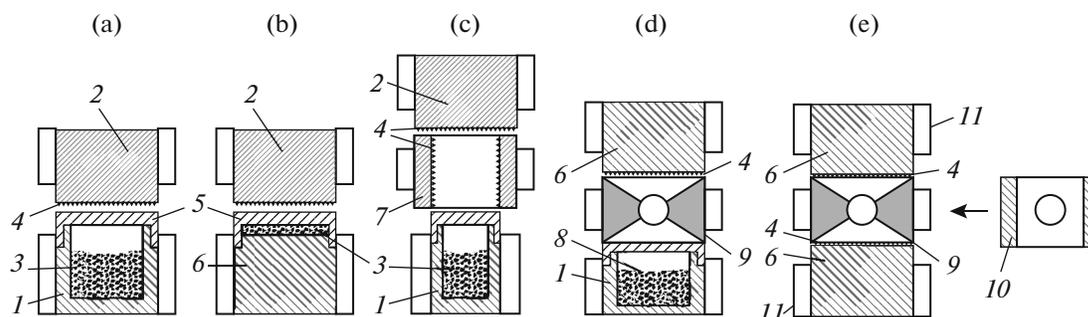
Fig. 1. Graphite crucible and rod atomizers with zones of evaporation–condensation of elements for sample preparation of solid suspensions. (a, b, c) Crucible and rod evaporator–collector systems for the thermal decomposition of solid samples and the fractional evaporation–condensation of elements: (a) crucible with a diaphragm–rod; (b) rod with a diaphragm–rod; (c) crucible–cylinder–rod. (d, e) Atomizers–evaporators for simultaneous analysis of a thermally modified sample and condensate or two condensates: (d) crucible–cell–rod; (e) rod–cell–rod. (*1*) Crucible (evaporator); (*2*) rod (collector); (*3*) solid sample of suspension; (*4*) condensate (concentrate); (*5*) graphite diaphragm–filter; (*6*) rod (evaporator); (*7*) cylinder (collector); (*8*) thermally modified sample; (*9*) graphite cell with an illuminated hole (analytical zone); (*10*) simpler modification of the cell without vapor localization in the analytical zone; (*11*) exchangeable cooled holders of electrical contacts of the atomization unit.

(ashing) in an atomizer, usually at a temperature no higher than 450–550°C. However, the conventionally used ashing procedure does not allow the researcher to necessarily diminish the effect of the matrix composition to directly analyze ultratrace concentrations of elements.

A promising approach is to preliminarily separate or concentrate the elements by means of selective fractional evaporation when the solid sample is heated to a higher temperature. This sample-preparation procedure was fairly frequently successively employed in atomic emission (AA) analysis (Zil'bershtein et al., 1971) and was tested in AA analysis of samples of complex composition (Oreshkin and Tatsii, 2010; Oreshkin and Tsizin, 2012, 2013; Zakharov et al., 2012; Nagulin et al., 2012). The main difficulties thereby stem from the necessity for modernizing the design of the atomizers to conduct the thermal treatment of the samples and the fractional evaporation–condensation of their chemical elements.

In this publication we suggest means to preparatorily thermally treat the sample in the specialized crucible and rod atomizers themselves in the course of analysis of riverine and marine suspensions for Ag, Cd, and Tl.

EXPERIMENTAL

The experiments were carried out in a Saturn-2 (Russia) AA spectrophotometer with a deuterium background corrector and a modified experimental atomization unit, which is described in (Oreshkin et al., 1990). The unit can also be mounted on AA spectrophotometers of other types currently utilized in geochemical studies. Graphite crucible and rod atomizers (sample evaporator–condensate collector units) (Fig. 1) were fixed the between electric-contact holders of this unit. In our experiments, crucibles, rods,

cylinders, and cells 5–12 mm high were used, whose inner diameter was 4.5–8 mm, the inner diameter of the crucible was 3–5 mm, and that of the cylinder was 4–6 mm. The analytical zone in the cell was 2.5–4 mm in diameter. The thickness of the porous diaphragm-filter was 0.3–0.5 mm. The spacing between the evaporator and collector was regulated to be 0.5–2 mm. The graphite evaporators and collectors were preparatorily annealed at temperatures of ~2300–2500°C to get rid of possible contaminants. The radiation sources were hollow-cathode lamps and high-frequency electrodeless ball lamps. The analytical signals were measured by integral and pulsed methods (Ag 328.1, Cd 228.8, and Tl 276.8 nm).

The analyzed samples of riverine suspensions were borrowed from a collection of samples from the Oka River, Prioksko–Terrasny Biosphere Reserve, which are most commonly used by researchers worldwide (Gordeev, 2012). The samples were collected in 2008 and 2013 using polyethylene vessels, away from riversides, from depths of 0 to 0.5 m. The membrane filtration was carried out in compliance with the requirements for geochemical studies (Gordeev, 2012; Gordeev and Oreshkin, 1990). In our experiments, we also utilized samples from collections of marine suspensions that were previously analyzed by a number of techniques (Gordeev and Oreshkin, 1990, Oreshkin and Tsizin, 2003). Circles 3–5 mm in diameter were cut off different parts of the membrane filter with a suspension sample on it and placed into a graphite crucible (four to eight circles) or between the graphite rod and diaphragm (one to three circles) (Figs. 1a, 1b). If the mass of the suspension was greater and could be separated from the filter, such samples were diluted with graphite powder in the ratios of 1 : 1 or 1 : 5, and 1–6 mg of the material were loaded into the crucible. The crucible was also used to thermally treat the concentrates (3–5 mg) obtained by adsorption of elements
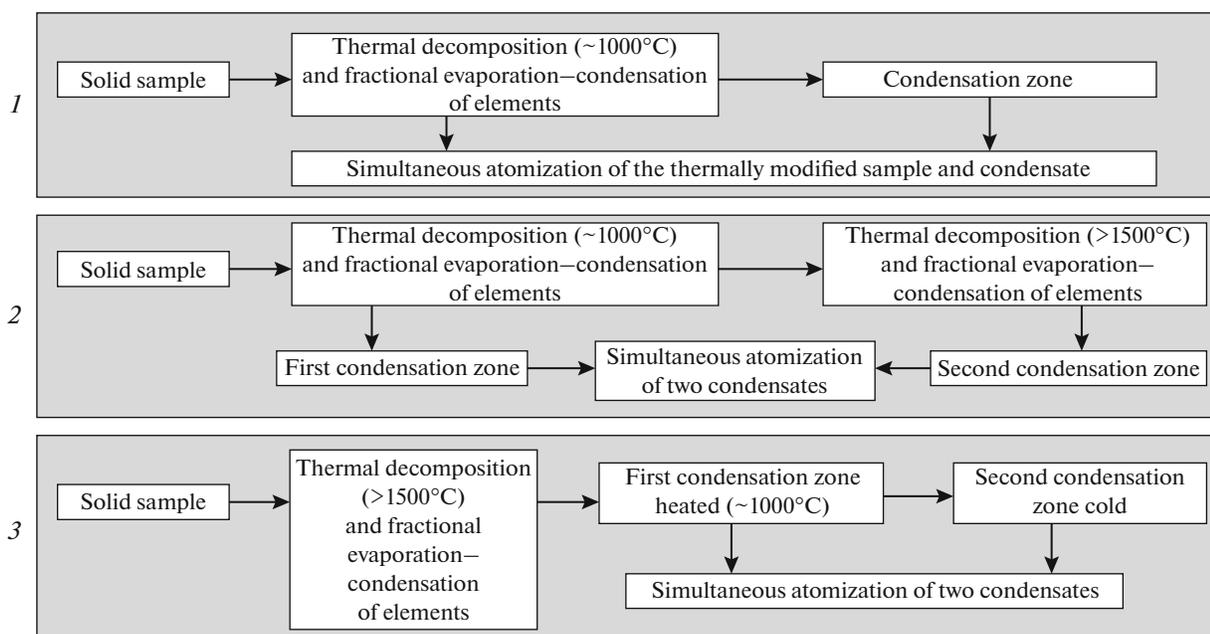
Fig. 2. Flow diagrams for various scenarios of the "pure" sample preparation procedure for solid samples of suspensions in crucible and rod atomizers with evaporation–condensation zones. (*1*) Sample preparation involving a low-temperature stage of the thermal decomposition and fractional evaporation–condensation of elements for the subsequent atomization of the thermally modified sample and condensate. (*2*) Sample preparation involving two successive stages of low- and high-temperature thermal decomposition and fractional evaporation–condensation of elements for subsequent simultaneous atomization of two condensates. (*3*) Sample preparation involving a high-temperature thermal decomposition and fractional evaporation–condensation of elements for subsequent simultaneous atomization of two condensates.

on DETATA adsorbent after the decomposition of the mixture (Oreshkin and Tsizin, 2003). To calibrate the dependences, we placed reference samples (solutions with known concentrations of an element were introduced into natural samples, pure membrane filters, and graphite powder) into the atomizer-evaporators. Before the experiments, all the samples were stored in hermetically sealed Teflon capsules.

The low-temperature (1000°C, 30–40 s, gradual heating) and high-temperature (1600–190°C, 10–20 s, gradual heating) thermal decomposition of the samples and the selective evaporation–condensation of elements (Fig. 2) were carried out in the systems of crucible with a diaphragm–rod and a rod with a diaphragm–crucible (Fig. 1). The systems of a crucible with a diaphragm–cylinder–rod and a rod with a diaphragm–cylinder–rod were used to conduct only the high-temperature thermal decomposition with condensation of elements in the first condensation zone (in cylinder) heated to 1000°C and in the second condensation zone on the rod (cold). If only the low-temperature stage was used (for marine suspensions), the thermally modified sample and condensate were analyzed in a three-chamber crucible–cell–rod atomizer (Fig. 1d); in two successive stages (riverine suspensions), two condensates were analyzed in a rod–cell–rod atomizer (Fig. 1e). Condensates in the cylinder and on the rod (Figs. 1c) were analyzed after a single high-temperature stage (riverine suspensions sampled

in 2013) either in an atomizer of the cylinder–cell–rod type (Oreshkin and Tsizin, 2012) or, after re-evaporation of the condensate onto the rod, in a rod–cell–rod atomizer (Fig. 1). The atomization temperature of the matrixes was 1700–1900°C (3–6 s). Elements were evaporated into the isothermal analytical zone in the cell, which was heated in advance (Sr values are usually lower than 0.25).

RESULTS AND DISCUSSION

Direct atomic absorption (AA) analysis does not require sample preparation, but instead a "pure" sample preparation is applied: the sample is thermally treated (ashed) immediately in the atomizer, and thus, the risks of contamination or losses of the elements to be analyzed significantly reduced. Direct AA analysis of solid samples is carried out in electrothermal atomizers of various types (Pupyshev, 2009). A specialized atomizer for the analysis of solid samples is a graphite crucible, which originally has found application in the AE method (Zil'bershtein et al., 1971). The use of a single-chamber crucible for the direct AA analysis of suspensions generally has little success because of the high levels of unselective and matrix interference. It is more efficient to use a two-chamber crucible–cell atomizer (Oreshkin et al., 1986, 1990, 1994) with an isothermal analytical zone (the well-known principle of the L'vov graphite platform). However, thermal

treatment of suspensions at temperatures of 400–500°C does not sufficiently eliminate the effect of the sample composition when elements (Ag, Bi, Cd, Tl, etc.) should be analyzed accurate to $n \times 10^{-7}$ to $n \times 10^{-6}\%$. Moreover, losses not only of Hg but also of other elements (Cd, Pb, and Tl) were detected to occur during the ashing stage. Obviously, a stage of preliminary sample preparation with the separation/concentration of elements was needed. This put forth the problem of the possibility of carrying out this stage in the atomizer itself. For example, elements were concentrated on a DETATA adsorbent in the crucible–microcolumn from solutions after the decomposition of the suspension (Orfeshkin et al., 2002; Oreshkin and Tsizin, 2003).

An alternative and highly promising approach does not employ a chemical preparation of the sample. Previously, AE analysis was often conducted using selective fractional separation/concentration of volatile and medium-volatile elements at heating solid samples in a graphite crucible to a temperature of 1500–2000°C (Zil'bershtein et al., 1971). The crucible is a part of the system of a heated sample evaporator and an unheated condensate collector. The additional fractional concentration of elements on a specialized collector surface during the sample preparation cycle practically always facilitates a significant reduction of the influence of the sample composition and the losses of elements during the thermal decomposition of organic components. Note that riverine and marine suspensions sometimes contain up to 10–50% (and even more) organic matter (Gordeev, 2012). If not modified, currently used models of electrothermal atomizers (Pupyshev, 2012) cannot be applied for such sample preparation. The usable ones are modernized crucible and rod atomizer evaporator–collector systems and ones for direct analysis of thermally modified matrixes (Figs. 1a, 1b, 1d. 1e) and those proposed herein (Figs. 1c). In AE analysis, the fractional evaporation of the samples and condensation of elements is conducted using a simple enough system of crucible (evaporator of the solid sample) and an electrode or cap (condensate collector) (Zil'bershtein et al., 1971). We applied a modification of this system (crucible with a diaphragm–rod, Fig. 1) in the course of this research for preparing samples of suspensions or DETATA concentrates. The rod with a diaphragm–rod system is targeted for the thermal treatment of small amounts of suspensions. The porous graphite diaphragm does not allow particles and aerosols to come to the condensation zone. As a result, condensate (concentrate) of elements was obtained on the surface of the collector rod. However, significant technical difficulties, such as previously noted in (Zil'bershtein et al., 1971), occurred during the thermal decomposition of mineral-organic suspensions and the fractional evaporation–condensation of elements at evaporator temperatures above 1500°C. These difficulties stemmed from the need to effectively cool the condensation zone, which occurs near the evaporator. Thereby losses of elements, which are hard to control, are possible. In view of this, alternative means of sample thermal treatment were suggested: a stage of the thermal decomposition of the samples and fractional evaporation–condensation is divided into two separate stages (low-temperature at ~1000°C and high-temperature at >1500°C ones) (Fig. 2). The temperature of the former stage is much higher than that recommended for ashing of mineral-organic samples without modifying reactants. Experiments have demonstrated that a single low-temperature stage can be used in analysis of elements in marine suspension samples rich in organic matter and also in a homogeneous DETATA concentrate matrix. The latter variant of thermal treatment involves two successive stages with independent rods (condensate collectors): low- and high-temperature ones (Fig. 2). Obviously, these approaches can be implemented only at the subsequent simultaneous atomization of the spatially separated matrixes (in the crucible and on the rod) in specialized three-chamber crucible–cell–rod and rod–cell–rod atomizers (Figs. 1d, 1e). These atomizers have two independent evaporation zones (the crucible and rod or two rods) and a common isothermal atomization zone (analytical), which are independently heated. Hence, it is possible to simultaneously analyze a thermally modified sample and a condensate or two condensates.

The most promising (although technically more complicated) variant of sample preparation (Fig. 2) involves a single high-temperature stage of the thermal decomposition of the suspensions and the fractional evaporation–condensation of elements. A basic design is suggested for the system of a crucible with a diaphragm–cylinder–rod with two condensation zones (Fig. 1c). In this design, the crucible-evaporator is substituted for a rod-evaporator to obtain a system of a rod with a diaphragm and a cylinder-rod. A distinguishing feature of such systems is that the first condensation zone in the cylinder is heated (~1000°C), and the second one, on the rod surface, is "cold". The second condensation zone is situated close to the cylinder, whose temperature is much lower than the temperature of the crucible. The vapor of elements is condensed on the cylinder surface and partly on the rod surface. The heated intermediate condensation zone in the cylinder facilitates the more complete thermal decomposition of the volatile compounds. This design makes it possible not only to diminish the losses of elements but also to increase the evaporation temperature of the sample, i.e., reach a higher degree of atomization of matrix components. The crucible and rod atomizers of modernized design are thus multifunctional and are purposed to the preparatory thermal treatment of solid suspensions, involving stages of the separation/concentration of elements by means of selective fractional evaporation in the working volume itself. Experiments have proved the efficiency of these

Table 1. Concentrations (ppm) of elements in riverine suspension analyzed by various techniques

Component	Ag		Cd		Tl	
	1	2	1	2	1	2
Oka R., May, 2008 May, 2013	0.044 ± 0.007 0.080 ± 0.010 (0.073 ± 0.08)	0.052 0.061	0.57 ± 0.06 0.38 ± 0.05 (0.30 ± 0.05)	0.20; 0.45 0.31 ± 0.05	0.90 ± 0.20 1.1 ± 0.3 (0.78 ± 0.08)	1.3 ± 0.3
Oka R., June, 2008 June, 2013	0.067 ± 0.009 0.086 ± 0.007 (0.09 ± 0.01)	<0.1 0.077	0.80 ± 0.10 1.2 ± 0.2 (1.0 ± 0.1)	0.75 1.4 ± 0.3	0.40 ± 0.10 1.3 (1.2 ± 0.2)	0.05 1.0
Oka R., July, 2008	0.15 ± 0.03	0.12 ± 0.02	1.1 ± 0.3	0.09 ± 0.03	0.71 ± 0.07	0.88 ± 0.12
Oka R., September, 2008 September, 2013	0.16 ± 0.03 0.05 ± 0.01 (0.054 ± 0.006) [0.14 ± 0.02]	0.19 ± 0.04 0.06 ± 0.02	0.92 ± 0.15 0.17 ± 0.04 (0.14 ± 0.03) [0.71 ± 0.08]	1.0 ± 0.2 0.20 ± 0.05	1.2 ± 0.3 0.35 ± 0.06 (0.29 ± 0.04) [0.90 ± 0.10]	0.70 ± 0.10 0.36 ± 0.05
G−2 (granite) internationally certified standard	0.034 0.040[a]	–	0.023 0.016[a]	–	1.1 0.91[a]	–
Average for riverine suspension[b]	0.3	–	0.5	–	0.56	–
Atlantic Ocean[c]	0.045	0.040	0.12	0.16	0.31	0.60
Atlantic Ocean[d]	0.11	0.075	0.28	0.21	0.53	0.39
Central Pacific Ocean[e]	0.030	–	0.018	0.010	0.13	0.20

(1) Analysis with fractional selective concentrating (systems (a) and (b), numerals in parentheses are system (c) Fig. 1, numerals in brackets are analyses with introduction of elements: 0.1 ppm Ag, 0.5 ppm Cd, Tl; (2) analysis after concentrating on DETATA adsorbent (the year 2008 is a static variant outside the atomizer, and the year 2013 is a dynamic variant in a crucible−microcolumn) (Oreshkin et al., 2002; Oreshkin and Tsizin, 2003); [a] Govindaraju, 1989; [b] Savenko, 2006; [c, d] (c) near and (d) away from the mouth of the Amazon River (Gordeev and Oreshkin, 1990); [e] Oreshkin and Tsizin, 2003.

"unusual" systems in the sample-preparation cycles of suspensions to be analyzed for trace amounts of elements (there are no "usual" systems for this purpose). The suggested thermal-treatment procedures (Fig. 2) can be classed with the type of "pure" ones because they do not require the use of any reactants and procedures in chemical vessels. It is also worth mentioning that the graphite atomizers can be easily cleaned by annealing.

The suggested approaches are applicable in AA analysis of riverine and marine suspensions. As an illustrative example, Table 1 presents analyses of riverine and marine suspensions for Ag, Cd, and Tl. It is fairly difficult to directly analyze these elements because of matrix effects. Previously, samples of this type were preparatorily dissolved, elements were concentrated on DETATA adsorbent, and the concentrate was then directly analyzed (Oreshkin et al., 2002; Oreshkin and Tsizin, 2003). These methods were also applied in this research. To control the accuracy of the results, replicate analyses for the elements were carried out using the internationally certified standard G-2

(granite) and a sample of riverine suspension, with the additional introduction of elements.

Most of the results are generally reasonably well consistent, although some inconsistencies were also detected (a certain role was likely played by the heterogeneity of suspension distribution on the filters). In two samples of riverine suspensions, data on Cd (July 2008) and Tl (June 2008) are remarkably different. Losses of elements likely occurred during the stage of dissolving the sample, concentrating the elements under static conditions outside the atomizer, and separating the concentrate by filtering. The suggested technologies make it possible to simplify the sample preparation procedures and diminish the risks of contamination of the sample and losses of the elements (these technologies are thus preferable to be applied in geochemical studies). In conclusion, it is worth mentioning the fact that Ag concentrations in samples of riverine suspensions (from the middle reaches of the Oka River) are notably lower than the clarke values (Savenko, 2006). Although the data are still scarce, it can be concluded that the average Ag and Cd concentrations in the riverine suspensions in the year 2008 were 1.5 times higher than in

the year 2013: 0.11 versus 0.070 ppm Ag and 0.85 versus 0.57 ppm Cd. The Tl concentrations did not vary: 0.81 versus 0.82 ppm.

CONCLUSIONS

Crucible and rod atomizers with evaporation−condensation zones of elements enable "pure" preparatory thermal treatment of solid riverine and marine suspensions. Variants are suggested for the low- and high-temperature thermal decomposition of solid samples and for the selective fractional evaporation−condensation of elements in specialized atomizers: crucible and rod systems of an evaporator and collector. If conducted in the working volumes of atomizers, these procedures enable reducing the risks of contamination and losses of elements and allow reducing matrix effects during the final stages of atomization. Elements (Ag, Cd, and Tl) were analyzed in riverine suspension samples for purposes of ecological−geochemical control.

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