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Analytical note

Determination of gold and cobalt dopants in advanced materials based on tin oxide by slurry sampling high-resolution continuum source graphite furnace atomic absorption spectrometry

Daria G. Filatova [a,*], Vasilina V. Eskina [b], Vasilisa B. Baranovskaya [c], Svetlana A. Vladimirova [a], Alexander M. Gaskov [a], Marina N. Rumyantseva [a], Yuri A. Karpov [c]

[a] Lomonosov Moscow State University, Faculty of Chemistry, Leninskiye Gory 1-3, GSP-1, Moscow 119991, Russia
[b] National University of Science and Technology "MISIS", Leninskiy prospekt 4, Moscow 119049, Russia
[c] Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Leninskiy prospekt 31, Moscow 119991, Russia

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ABSTRACT

A novel approach is developed for the determination of Co and Au dopants in advanced materials based on tin oxide using high-resolution continuum source graphite furnace atomic absorption spectrometry (HR CS GFAAS) with direct slurry sampling. Sodium carboxylmethylcellulose (Na-CMC) is an effective stabilizer for diluted suspensions. Use Na-CMC allows to transfer the analytes into graphite furnace completely and reproducibly. The relative standard deviation obtained by HR CS GFAAS was not higher than 4%. Accuracy was proven by means inductively coupled plasma mass spectrometry (ICP-MS) in solutions after decomposition as a comparative technique. To determine Au and Co in the volume of SnO_2, the acid decomposition conditions (HCl, HF) of the samples were suggested by means of an autoclave in a microwave oven.

1. Introduction

Nanocrystalline materials based on tin oxide are widely used as sensitive materials for gas sensors [1].To improve the selectivity of these semiconductor oxides, their surface is modified to create complex systems by introducing into the highly dispersed oxide matrix catalytic dopants: platinum group elements or oxide catalysts [2]. The distinct feature of these methods is a great difference in quantity of components in the final product and quantity of the precursor. In this regard, the investigation of methods for determining the composition of the materials obtained in various ways is of exceptional importance for the establishment of the relationship "the conditions of synthesis—functional properties". At the same time, one of the problems is the absence of standard reference materials for validation of analytical data. The synthesized tin dioxide modified by cobalt impregnation and gold by anion adsorption. The use of Co_3O_4 as a modifier is of interest, since this compound can act as a catalyst for oxidation reactions. The introduction of a gas sensitive layer of Au (also an effective oxidation catalyst) is a method of increasing the sensitivity to gases with reducing properties. Earlier we proposed methods for determining dopants in tin dioxide in the solutions after decomposition, however, these materials can be hardly decomposed, therefore it is more convenient to analyze solid samples [3,4].The main advantages of the high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GFAAS) are the sensitivity, the simplicity and no sample treatments are necessary. Thereby this method was actively used to analyze various materials recently [5–10]. It should be noted that as the matrix consists of tin, direct solid sampling for investigated materials was impeded. On the other hand, the selection of sample mass for direct solid sampling is limited by 0.1 mg [11,12]. The solution for this problem can be found by preparation of diluted suspensions with subsequent slurry sampling into a graphite furnace. Similar methods are often used [13,14]. However, to prepare stable sample suspensions it is necessary to search for a stabilizing reagent. Sodium carboxylmethylcellulose (Na-CMC) is used for stabilizing nanoparticles with diameter <17 nm [15]. It is shown that the produced suspensions have lower viscosity and longer sedimentation times at low content Na-CMC [16]. These advantages of Na-CMC can be used to produce dilute suspensions of our samples. The application of this reagent was not discussed for subsequent determination by HR-CS AAS. There is no research on the quantification of cobalt and gold by HR-CS AAS in advanced materials based on tin oxide. Hence, this work describes the development of HR-CS GFAAS for the determination of Co and Au in semiconductor gas sensors based on tin oxide by slurry sampling. We have already obtained data on the distribution and quantification of cobalt in materials by inductively

* Corresponding author.
E-mail address: gak1.analyt@gmail.com (D.G. Filatova).

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coupled plasma mass spectrometry (ICP-MS) in solutions after decomposition [17]. The suggested approach will be used for validation of the results for Au and Co.

2. Materials and methods. Instrumentation

2.1. Analytical procedures

2.1.1. HR-CS GFAAS

Investigations were carried out using an atomic absorption spectrometer ContrAA 600 with a continuum spectrum source developed by Analytik Jena AG (Jena, Germany), resolution of $\lambda/\Delta\lambda = 145{,}000$, which corresponds to a spectral bandwidth of <2 pm/pixel at 200 nm [18].

The atomizer for the liquid sample is injected by means of the micro pipette unit MPE 60 (Analytik Jena AG, Jena, Germany). Argon (99.998%, NII KM, Moscow, Russia) was used as a purge and protective gas. The instrumental parameters were created with consideration for the recommended conditions for analytical methods on the ContrAA 600 device [18, Table S1 (Appendix)].

2.1.2. ICP-MS

Measurements by ICP-MS were performed on an Agilent 7500C inductively coupled plasma quadrupole mass spectrometer (Japan). The spectrometer was controlled with a PC using the ChemStation (version G1834B) software package (Agilent Technologies). Measurements were performed for isotopes ^{197}Au, ^{59}Co and $^{118,\ 120}$Sn.

2.1.3. Preparation of suspensions

The powders of nanocomposites were synthesized at different temperatures, from 300 to 700 °C. Samples of materials were introduced into the graphite furnace as suspensions without decomposition. According to the synthesis conditions, the size of the particles of SnO_2-Au/Co_3O_4 was 60–80 nm. The suspensions were obtained by adding sodium carboxylmethylcellulose (Sigma-Aldrich, USA) solutions to powders. Low (grade C5678, 50–200 mPa × s, 4% in H_2O (25 °C)) and medium (grade C4888, 400–800 mPa × s, 2% in H_2O) viscosity Na-CMC are used as suspending agents. The suspensions obtained were treated in an ultrasonic bath for 15 mins. Rotary viscometer Brookfield LVDV-II +, USA was used for the viscosity measurements.

2.1.4. Samples' preparation and standard solutions

For the digestion of samples, a mixture of acids of 1 mL of HCl, 1 mL of HNO_3 and 1 mL of HF (all reagent of analytical grade Merck, Germany) were added to the weighed 0.0020 g of the samples. Then the samples were placed into an autoclave in a microwave oven for 1 h. Microwave oven MARS 5 microwave accelerated reaction system with 12 XP 1500 Plus high pressure vessels (CEM, United States). The working frequency of the system was 2455 MHz, radiated power was 1600 W.

Standard solutions of Au, Co and Sn with concentration 1.0; 2.5; 50; 100; 200; 300; 400; 500 μg L^{-1} were prepared for the creation of calibration schedules from the standard solution (High-Purity Standards, Charleston, SC, USA) with concentrations of the determined elements of 10 mg L^{-1}. Calibration solutions were prepared by serial dilution of the initial solutions with deionized water (Millipore, 18.2 mQ/cm). The solution of the control sample was used for the measurement of the background signal. The determination of elements was carried out by means of calibration schedules of dependence of absorption signals from concentrations.

The accuracy of the determination of gold, cobalt and tin in powders of nanocomposites by HR CS GFAAS was confirmed by their determinations in solutions after decomposition by ICP-MS. The accuracy of the determination of gold, cobalt and tin by ICP-MS was confirmed by their determinations in solutions of model mixtures containing corresponding amounts of elements. The selected ratios correspond to real samples of nanocomposites: 0.2% wt. Au and 3% wt. Co in SnO_2. The relative standard deviation (RSD) was 5 and 6% for Au and Co, respectively.

3. Results and discussion

3.1. Preparation of stable suspensions for the samples SnO_2-Au/Co_3O_4

The use of Na-CMC allows for the transfer of the insoluble substances in an aqueous solution into a stable, finely dispersed state, since the reagent forms hydrophilic monomolecular protective layers around individual particles. Stability of the suspensions was studied in the concentrated solutions of samples (1 mg of the material was weighed and 5 mL of the reagent was added) by the accumulation of a precipitate. The aggregate and sedimentation stability of the resulting systems is achieved by means of the distribution of particles between layers of Na-CMC.

Table S2 (Appendix) presents the stability of the results of the suspensions depending on the type and concentration of Na-CMC.

According to the received data, the Na-CMC grade C5678, 0.2% wt and C4888 0.2% wt can be used for the preparation of stable suspensions. We selected a reagent with low viscosity C5678, 0.2% wt, to reduce the influence of viscosity on sampling by a capillary.

3.2. Determination of gold and cobalt in the presence of tin in model solution

The model mixture contains the same amounts of elements as the sample. The selected ratios correspond to real samples of nanocomposites: ≈0.2–0.3% wt. Au and ≈3% wt. Co in SnO_2. 1.6 μg L^{-1} Au, 20 μg L^{-1} Co and 500 μg L^{-1} Sn were in the solution during the analysis. It should be noted that Au samples should be acidified with 0.5% (m/v) HCl to keep element in solution. Using the example of a standard solution, we showed that the tin signal is decreased in the presence of HCl. This happens due to the formation of volatile chloride compounds of tin in a graphite furnace. Therefore, the solution of the mixture was prepared with the use of HNO_3. The changes of the signal of gold were not observed as when compared to the chloride solution. According to the obtained results (Table 1), there is the possibility to determine Au, Co and Sn in model samples with a relative standard deviation (RSD) of 3, 4 and 3%, respectively.

We identified the analytes without interelemental influences (Fig. S1 (Appendix)). It can be seen from the data that the peak of cobalt is broadened due to the large content of the element. However, this did not influence the results of the determination. The limits of quantitation (LOQ) that were achieved by HR CS GFAAS were 0.7 μg L^{-1} for Au and 0.6 μg L^{-1} for Co in the presence of tin overage.

3.3. The influence of Na-CMC on the determination of gold, cobalt and tin in a graphite furnace

The standard solutions of Au, Co and Sn were prepared with 0.2% wt C4888 for evaluation and took into account the effect of Na-CMC on the determination of analytes. We could not detect the signals of analyte due to the formation of a strong fuming flux under conditions that are recommended by the software of the device. We used two subsequent

Table 1
The results of determination of gold, cobalt and tin in model solutions by HR CS GFAAS (1 − a = 0.95, n = 5).

Analyte	Introduced, μg L^{-1}	Found, μg L^{-1}
Au	1.6	1.60 ± 0. 05
	1.2	1.20 ± 0. 04
Co	20	20.0 ± 0.8
	15	15.0 ± 0.6
Sn	500	500 ± 16
	400	400 ± 11