DETERMINATION OF MERCURY AND COPPER TRACES IN ULTRAPURE SPECTRAL CARBON BY DPASV ON A GOLD-FIBRE MICROELECTRODE

Miroslav RIEVAJ, Štefan MESÁROŠ and Dušan BUSTIN*

Department of Analytical Chemistry,
Slovak Technical University, 812 37 Bratislava, The Slovak Republic

Received June 16, 1993
Accepted September 5, 1993

A simple and sensitive method is proposed applying a gold fibre microelectrode for the DPASV determination of Hg and Cu traces in an ultrapure spectral carbon. The procedure allows simultaneous determination of both elements at the purity level lower than 1 . 10^{-6} wt.%. Two different sample preparation techniques – ashing in stream of oxygen, and elution with a mixture of concentrated HCl and HNO_3 – were applied for releasing the metals spread in carbon matrix. Testing of the digestion techniques with synthetic Hg and Cu spiked samples proved both to be satisfactory. The proposed determination has a sensitivity high enough to verify the required highest purity level of the spectral carbon as concerns Hg and Cu traces.

For a commercially available ultrapure spectral carbon a purity level down to 1 . 10^{-6} wt.% is sometimes requested. To analyze metal impurities at such a low level, not only atomic absorption spectrometry (AAS) but also electroanalytical procedures based mainly on differential pulse anodic stripping voltammetry (DPASV) were reported for various types of samples. While for the majority of them (Cd, Pb, Tl, Zn, Sb, Bi) mercury was found to be the most suitable electrode material for their determination[1] (either as a hanging mercury drop or a mercury film on a glassy carbon), for Hg necessarily[2] and Cu preferably[3] (due to certain difficulties connected with the limited solubility of Cu in Hg) a gold electrode was used. Pure gold as the most frequently recommended material for the determination of both metals was also applied in the present report. It was used for the construction of a gold-fibre microelectrode. Such an electrode possesses another advantageous property originating from its microelectrode character – the possibility of the accumulation in a stagnant solution. This enables to use a much simpler instrumentation and a more convenient performance of stripping

---

* The author to whom correspondence should be addressed.

analysis, nevertheless, the results are comparable to (or even better than) those obtained with conventional-size electrodes[4].

EXPERIMENTAL

Chemicals

All the chemicals were of analytical purity grade and were used without further purification. None of the reagents used contained Hg or Cu at a level providing detectable DPASV signals. The 1 . 10^{-4} mol dm^{-3} stock Cu^{2+} and Hg^{2+} solutions were prepared by dissolution of calculated amounts of Cu and HgO in concentrated HNO_3 and adjusting the exact volume with three times distilled water. The 2 . 10^{-6} mol dm^{-3} standard Hg^{2+} and Cu^{2+} solutions were prepared from the stock solutions by dilution every day.

Instruments

The DPASV measurements were carried out on a PA4 polarographic analyzer (Laboratorní přístroje, Prague) using a configuration of two electrodes. The construction of the working gold-fibre microelectrode and its pretreatment were described in detail in our previous paper[5]. The reference saturated calomel electrode (SCE) was connected to the sample solution by a salt bridge containing 1 mol dm^{-3} H_2SO_4 (exchanged daily). The method of exchanging of the solution was applied to optimize the signals formation during anodic stripping. The solution exchange was carried out without switching off the instrument. The working electrode was removed from the sample solution first, it was rinsed with distilled water and submerged in the exchanged solution (0.1 mol dm^{-3} $HClO_4$ + 0.003 mol dm^{-3} HCl) after the reference electrode. The scan rate of anodic stripping was 50 mV s^{-1}, the pulse height 50 mV, and the pulse frequency 5 Hz.

Preparation of Sample Solution

Two different procedures of preparation of the sample solution were used. The first one involved ashing of the carbon matrix in a stream of oxygen and dissolving the solid residue containing the metals determined in concentrated HNO_3. Usually 5 g of the analyzed ultrapure spectral carbon were slowly and carefully burned in a mild stream of oxygen (from a capillary). The combustion was performed in a heated silica-glass tube until the black carbon matrix turned into a white-gray ash. After cooling, the residue was dissolved in 2 ml concentrated HNO_3 and diluted to a volume of 10 ml with three times distilled water.

The second procedure is based upon the destruction of sorption properties of carbon matrix and extraction of both analyzed species with a mixture of concentrated HCl and HNO_3. In a typical experiment, 2 g of pulverized spectral carbon rod (crushed with a teflon bar in a teflon beaker) were extracted in an airtightly sealed teflon decomposition device[6] at 160 °C with 4 ml of the mixture $HCl-HNO_3$ (2 : 1) for two hours, cooled, filtered and finally the volume was adjusted to 10 ml with 3× distilled water.

RESULTS AND DISCUSSION

Preliminary Testing

The required purity level below 1 . 10^{-6} wt.% means a content of less than 10 ppb pollutants (Hg, Cu) in the ultrapure spectral carbon. It corresponds approximately to the concentrations of 2.5 . 10^{-8} mol dm^{-3} Hg^{2+} and 7.9 . 10^{-8} mol dm^{-3} Cu^{2+} in the sample solution if the "ashing" procedure described in Experimental is used. In the case of the "extraction" technique the corresponding Hg^{2+} and Cu^{2+} concentrations are 2.5 times lower. Respecting the above-mentioned concentrations levels, a series of synthetic samples with concentrations ranging from 1.6 . 10^{-8} mol dm^{-3} to 1.6 . 10^{-7} mol dm^{-3} Cu^{2+} and from 5 . 10^{-9} mol dm^{-3} to 5 . 10^{-8} mol dm^{-3} Hg^{2+} were prepared in the mixture 3 M (HCl + HNO_3) acids.

The determination of mercury at this concentration level caused no problems. This is due to the very advantageous potential +0.3 V vs SCE used for Hg electrodeposition at which very few potentially interfering electroactive species (including oxygen) are reduced. Therefore, the time-consuming de-aeration of the analyzed solution could be omitted. The mercury electrodeposition was performed in a stagnant solution due to the microelectrode character of applied working electrode[4]. After accomplishing Hg accumulation, the sample solution was replaced by the "exchanged solution" into which the anodic stripping was started by a polarization of the working electrode toward more positive potentials (the parameters are given in Experimental). The oxidation peak of mercury appeared at the potential of 0.6 V vs SCE. The polarization continued to 1.8 V vs SCE at which the electrode was conditioned for 1 min before the following analysis.

In the DPASV analysis of Cu the de-aeration (10 min) could not be omitted because the accumulation proceeded at −0.1 V vs SCE. The accumulation was again performed in a stagnant sample solution and anodic stripping of the deposited copper into the same "exchanged solution". The oxidation peak of Cu appeared at the potential ca 0.2 V vs SCE. The same procedure of the electrode conditioning as in the case of mercury was found to be appropriate.

The above-described preliminary experiments proved that the Hg and Cu determination can be performed in media similar to those arising after preparation of sample solution and at the mercury and copper concentration levels expected in analyzed sample solutions. Good reproducibilities were obtained. For reruns of the same sample, the peak heights of the stripping signals were within 10% reproducibility interval. The heights of anodic stripping peaks of both determined metals depended linearly on their concentrations in the whole above-mentioned concentration intervals. Their signals were also linearly dependent on the deposition time in the interval from 10 to 40 min for 2 . 10^{-8} mol dm^{-3} Hg^{2+} and 6 . 10^{-8} mol dm^{-3} Cu^{2+}.

Testing with Spiked Samples

The risks of both above-mentioned techniques of preparation of the sample solution must be taken into consideration. While in the case of ashing, the loss of the metals determined (especially mercury) during burning is threatening, in the extraction with acids certain amounts of Hg and/or Cu might escape and remain in the carbon matrix. The reliability and efficiency of both procedures were tested using Hg and Cu spiked synthetic samples. The calculated amounts of mercury and copper in the form of standard Hg^{2+} and Cu^{2+} solutions were added to the samples of the ultrapure spectral carbon

TABLE I

Results of analysis of synthetic Hg and Cu spiked samples of ultrapure spectral carbon

Spiked sample	Spiked amount given/found[a], ng g^{-1}		Standard deviation ng g^{-1}		Confidence interval for 95% probability, %	
	Hg	Cu	Hg	Cu	Hg	Cu
1	5.0					
	3.6		1.5		72 ± 49	
2	10.0					
	7.8		2.4		78 ± 36	
2[b]	10.0					
	8.3		2.2		83 ± 31	
3	20.0					
	15.8		4.1		78 ± 31	
4		5.0				
		4.2		1.3		84 ± 37
5		10.0				
		8.8		2.6		88 ± 35
5[b]		10.0				
		8.4		1.9		84 ± 27
6		20.0				
		18.2		4.4		91 ± 29
7	5.0	20.0				
	3.5	19.2	1.4	3.6	70 ± 47	96 ± 22
8	20.0	5.0				
	14.3	5.3	3.7	1.3	74 ± 31	106 ± 29

[a] Average of five determinations; [b] "extraction" sample solution (see Experimental).

with very low pollutants content (determined by atomic absorption spectroscopy, which was considered to be an independent method in this case). Only samples with the Hg and Cu content lower than 1/5 of the required limit were taken for spiking. The spiked samples were processed by both procedures. The multiple standard addition method was used for the evaluation of both metals.

The results of Hg and Cu analysis in the spiked samples are given in Table I. The statistical evaluation of experiments shows the arithmetic mean of parallel determinations does not differ statistically from the given Hg or Cu values in any of the spiked samples. The confidence interval is well acceptable taking into account low concentration levels of determined metals. Slightly lower found values, especially in the case of mercury when ashing procedure was applied, can be explained as a loss of the determined species as a consequence of the relatively high temperature during burning of the carbon matrix in the stream of oxygen. The found values of both Hg and Cu were slightly lower also when the extraction method of the sample solution preparation was applied. This was possibly caused by insufficient extraction. Nevertheless, the loss of mercury in this case was lower than that caused by the high temperature during carbon matrix burning. In spite of the above-mentioned problems both methods can be considered to be suitable for preparing the sample solution. Slight losses of the metals determined can possibly be taken into consideration for correction of the results of analysis.

Mutual interference of Hg and Cu was also investigated. As shown in Table I copper did not interfere when only Hg analysis was performed. At the potential of –0.1 V vs SCE necessary for copper deposition both metals are accumulated. Both metals can be simultaneously determined in this case. Their mutual interference was found to be negligible (Table I) when both of them were present in amounts expected for an ultrapure spectral carbon.

The signals corresponding to $4 \, . \, 10^{-9}$ mol dm^{-3} Hg^{2+} and $1.6 \, . \, 10^{-9}$ mol dm^{-3} Cu^{2+} (deposition time 40 min) can still be resolved from the background signals. These concentrations (corresponding approximately to 1/5 of the required level $1 \, . \, 10^{-6}$ %) can be considered to be an estimate of the determination limits of mercury and copper.

Real Sample Analysis

Hg and Cu were analyzed in rods of ultrapure spectral carbon by the same procedures as those described for the spiked samples. The results are given in Table II together with the values found by independent AAS method. Hg was determined using the cold-vapour atomic absorption spectrometric technique. The graphite-furnace atomic absorption spectrometry (direct thermal destruction of the sample solution used for DPASV analysis) was applied for Cu determination. As shown in Table II no significant difference was observed. The method, therefore, can be considered a less expensive alternative to the AAS analysis for monitoring both pollutants (Hg and Cu) in this ultrapure material at the required limiting level of 1 . 10^{-6} wt.%. In all analyzed samples of the ultrapure spectral carbon the content of the metals determined was below this rather strict purity level.

TABLE II
Content of Hg and Cu in ultrapure spectral carbon real samples[a]

Sample	Hg, ng g^{-1}				Cu, ng g^{-1}			
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
1	5.1	3.2	5.6	2.5[b]	4.9	3.1	6.1	3.2[b]
2	5.5	2.9	6.4	2.7[b]	5.7	3.3	5.6	2.8[b]
3	6.1	3.1			5.8	2.3		
4	7.4	2.6			6.8	2.7		
5	6.4	3.0			6.6	2.5		

[a] $\bar{x}$ Average of 5 measurements, s standard deviation; [b] determined by independent AAS method.

REFERENCES

1. Valenta P., Rutzel H., Krumpen P., Salgert K. H., Klahre P.: Fresenius Z. Anal. Chem. *292*, 120 (1978).
2. Sipos L., Valenta P., Nürnberg H. W., Branica M.: J. Electroanal. Chem. Interfacial Electrochem. *77*, 263 (1977).
3. Valenta P., Mart L., Rutzel H.: J. Electroanal. Chem. *82*, 327 (1977).
4. Wang J., Turhi P., Zadeii J.: Anal. Chem. *59*, 2119 (1978).
5. Rievaj M., Bustin D.: Analyst (London) *117*, 1471 (1992).
6. Rievaj M., Mesároš Š., Bustin D.: An. Quim. *89*, 347 (1993).

Translation revised by J. Panchartek.