Atomic Emission Method Developed for Determining Mercury Content in the Waste Adsorbents of Lithium Production

S. B. ZAYAKINA[1,2], L. M. LEVCHENKO[1] and V. N. MITKIN[1]

[1]*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)*

E-mail: sbz@che.nsk.su

[2]*Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Koptyuga 3, Novosibirsk 630090 (Russia)*

E-mail: zayak@uiggm.nsc.ru

Abstract

A direct atomic emission method developed for measuring mercury content in powder carbon adsorbents is shown to perform the simultaneous analysis of nuisance admixtures. It provides an express control of mercury content in carbon based modified adsorbents (CMA) used for mercury removal from wastewaters. Analysis accuracy is improved due to simultaneous calculations using several analytical lines of the element, mercury content range being 0.0001–1.0 mass %, admixture elements being detected at a content of $n \cdot 10^{-5}$ mass %.

INTRODUCTION

Carbon based modified adsorbent (CMA) was on purpose developed for mercury removal from the wastewaters at JSC "Novosibirsk Chemical Concentrates Plant" [1–5]. CMA using method was proved to provide at least 3 times higher mercury adsorption coefficient than other reported technologies [5–9].

In the present study we focus on the express method for determining mercury content in solid adsorbents and other solid wastes using atomic emission spectroscopy (AES).

We have shown [10] that excitation and spectrum registering conditions essentially influence the metrological parameters of the method. It is known [5] that d.c. arc can hardly be used for the AES mercury analysis. The reason is that mercury evaporation from the carbon anode channel is rather fast, and its vapors accumulate short-term in the arc discharge plasma, causing the self-reversal of spectral lines. Mercury emission stops in several seconds after the arc ignition. This complicates mercury analysis at photography registering [11]. Specially shaped electrodes, decelerating mercury entry into discharge plasma, somewhat increase the AES sensitivity towards mercury analysis [12]. However, this approach is not widely accepted.

New spectral excitation sources such as inductively coupled plasma (ICP), arc plasma sources, high frequency plasma sources and advanced registering and computation methods afforded new opportunity for mercury analysis. We have shown [13, 14] that automated arc two jet plasma source and diffraction spectrograph with multi channel emission spectra analysis (MESA) significantly widen the AES facilities for detecting a large set of elements within a $n \cdot 10^{-5}$ mass % concentration range.

EXPERIMENTAL

Analysis objects

AES method was used to analyze carbon adsorbents CMA or KAD [2, 3] used for the wastewater treatment. Mercury content in the wastewater varied from 0.001 to 5.0 mass %.

Reference samples

Standard mercury reference samples set SORt GSO 7183−95 (certified according to Rule 1286, 27.06.00) approved by the Russian Arbitrary Laboratory for Testing Nuclear Energy Materials at the Ural State Technical University.

Calibration plots for a wide set of elements were built using a set of 5 standard samples of graphite collector for micro admixtures (SOG-24) produced by the Russian Arbitrary Laboratory for Testing Nuclear Energy Materials at the Ural State Technical University. Standard reference samples contain Ag, Al, As, B, Bi, Cd, Co, Cr, Cu, Fe, Ga, Hg, In, Mg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Te, Tl (Table 1).

Apparatus

Automated setup including argon two-jet plasma source and diffraction spectrograph DFS-458 was described in detail elsewhere [13, 14]. For spectra registering MAES was installed in the spectrograph holder for the optical signal transformation into digital data for computer processing. Method software and analytical performance are discussed in [13, 15, 16]. For the purpose we upgraded spectrograph DFS-458 manufactured by the Kazan' Optical Mechanics Plant to improve the AES facilities,

TABLE 1

Content of each element in a set of reference samples SOG-24

Reference sample	Content, mass %
1	$1 \cdot 10^{-1}$
2	$1 \cdot 10^{-2}$
3	$1 \cdot 10^{-3}$
4	$1 \cdot 10^{-4}$
5	$1 \cdot 10^{-5}$

to expand the registered wave range and thus to increase the number of elements to be analyzed. According to our previous studies [17] spectrograph modernization improved the spectra quality, spectral range for lattice 1800 per millimeter being 190−368 nm. Wavelengths less than 230 nm were the most promising. Photo plates were not used due to their poor sensitivity. However, solid photodiodes proved to be efficient for emission detection in this particular spectral range.

Argon plasma temperature [18] and its stability in time are the guaranty of the mercury line excitation efficiency. It is well known that mercury spectral emission attains its maximum at an arc temperature of 6600−6800 K. Continuous sample introduction removes the fractionation effect. Both DFS-458 high optical efficiency and photodiodes sensitivity reduce exposure time to 6 s. This condition provides the required accuracy of mercury content determining in the solid adsorbents using the direct spectral methods.

In order to determine rather many other nuisance elements present in the sample we used the following optimized conditions: d.c. arc force 90 A, argon intake for plasma generation 2−3 l/min, for powder supply − 0.8 l/min, powder mass for single spectrum registering 50 mg.

Analytical signal registering

Method software [13−15] may use either line intensity I_l and continuous spectrum I_f or their difference $(I_l - I_f)$ as well as their ratio I_l/I_f as analysis signal. Since the line width exceeds the single diode size, one should consider several diodes when calculating intensities. Our program automatically chooses the appropriate set of diodes with the maximum intensity around the line. In case of DFS-458 spectral line expands over three or more diodes at a slit width of 20 mm. Integral intensity of lines is calculated according to formula [15]:

$$I_l = \sum_l i_{l+f} - (l/m)\sum_m i_f; \; I_f = (l/m)\sum_m i_f \qquad (1)$$

Here I_{l+f} is a signal of one diode under the line, l is the number of diodes required for the line, i_f is the signal of one diode for

TABLE 2

Parameters of lines for mercury analysis

λ, nm	Intensity	Critical	Detection limit*, mass %		Nuisance elements	
	(arc) [20]	potential, eV	DFS-8	ISP-30	λ, nm	Concentration, %
253.652	2000	4.89	0.01	0.03	Co I 253.596	>0.1
					Bi I 253.656	>3.0
312.668	200	8.85	0.5	1	Fe I 312.565	>10
313.845	200	8.84	0.5			

*Data [19] for evaporation from the direct current arch electrode.

background, m is the number of diodes taken to calculate the background. Spectrum parts to the line right and left free from hindering lines are taken for the background intensity estimation.

Energy and metrology parameters of the chosen set of mercury lines are given in Table 2.

Calibration plots and their parameters

In order to build the calibration plots and to estimate detection limits we registered 15−20 parallel surveys for each reference sample. With our software we statistically calculated preliminary (analytical signals) and final results, *i.e.* concentrations. In each case average value, standard deviation (s), and relative standard deviation (s_r) were calculated. Rough misses were rejected basing on the average values calculated with respect to desired s_r [21−24].

As it was mentioned above, our software allows analytical signal calculation with various methods. For the most sensitive Hg I line 253.652 nm we verified two calculation procedures. At first analytical signal was calculated according to formula (1). Then intensity amplitude was determined as:

$$I_{am} = (I_{\max, m} + 0.5\left|I_{m-1} - I_{m+1}\right|) - I_f \qquad (2)$$

Here m is the number of diode corresponding to the maximum line intensity. Figure 1 shows the registered distribution of line Hg I 523.652 nm.

For each calculation procedure we built calibration plots as log I − log C using standard linear equation: log $I = a_0 + a_1$log C [22, 23].

Our tests have shown that building calibration plot using the amplitudes of line intensities we obtain a slope angle of 53°. Therefore, calculated values are higher.
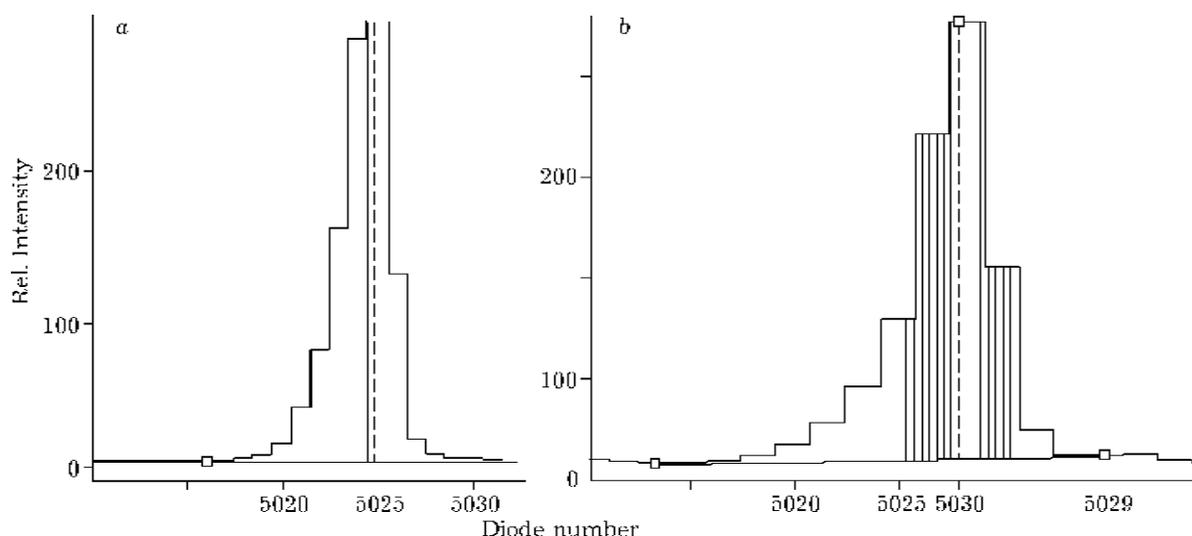

Fig. 1. Amplitude (*a*) and integral (*b*) intensities of Hg I line 253.652 nm. *Broken line* − analytical line centre.
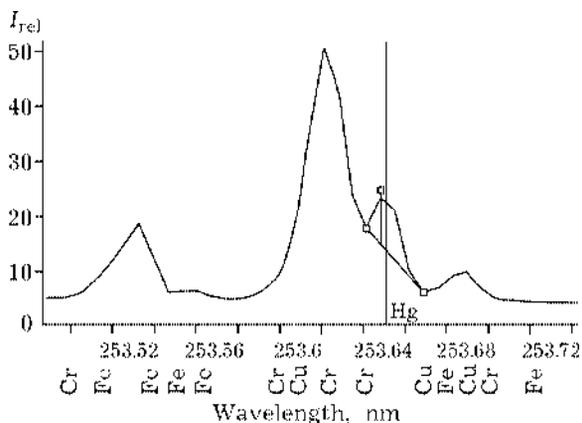
Fig. 2. Spectrum in a range of 253.5–253.7 nm.

Further on we used integral approach for analytical signal calculation, when building the calibration plots for the whole set of mercury lines.

Reference mercury containing CMA samples were as follows: CMA composition, mass %: C 99.0, O 0.86, H 0.11. Admixtures content, mass %: Ca 0.00014, Fe 0.02, K 0.017, Si 0.004, Mg 0.0023, Na 0.000018. Mercury content in the basic sample (Hg-1) was 1.13 %. Mercury was introduced as HgO. Reference sample Hg-2 was obtained by a 2-fold dilution of Hg-1 with CMA. Samples Hg-3 and Hg-4 were obtained by sequential Hg-2 dilution by 2-fold and 4-fold, respectively. Sample Hg-013 was prepared as Hg-1, but mercury was introduced as HgI_2, its content being 0.13 mass %.

All reference samples were found to fit the unified calibration plot independently of mercury introduction into the sample.

RESULTS AND DISCUSSION

Mercury content measurements have shown that analyzing several lines we improve the analysis accuracy, and essentially decrease and in some cases exclude the error caused by the imposition of admixture elements.

Analyzing mercury content in waste adsorbents [25–27] we have met the case, when the most intensive Hg I line 253.651 nm was hindered by the concomitant elements. Therefore, it could not be used for the mercury content measurements (Fig. 2). Spectrograph upgrade allowed us to use Hg II line 194.164 nm (Fig. 3).

AES method not only permitted the measurement of mercury content in a sample, but also the estimation of admixture composition in the waste adsorbent, *i.e.* lithium, calcium, sodium and potassium content. Typical parameters of calibration plots for the admixture metals and mercury are given in Table 3.

Using thus developed procedure we have analyzed 20 samples of waste adsorbent CMA-1, used for cleaning the acid wastewaters of lithium production. In Table 4 we summarize the data for several CMA-1 samples obtained with the AES (average value according to 4 lines) and AAS.

Contents of admixture metals such as lithium, calcium, sodium, and potassium in the n-th layer of adsorbent are shown in Table 5. Each element by two lines was analyzed (see
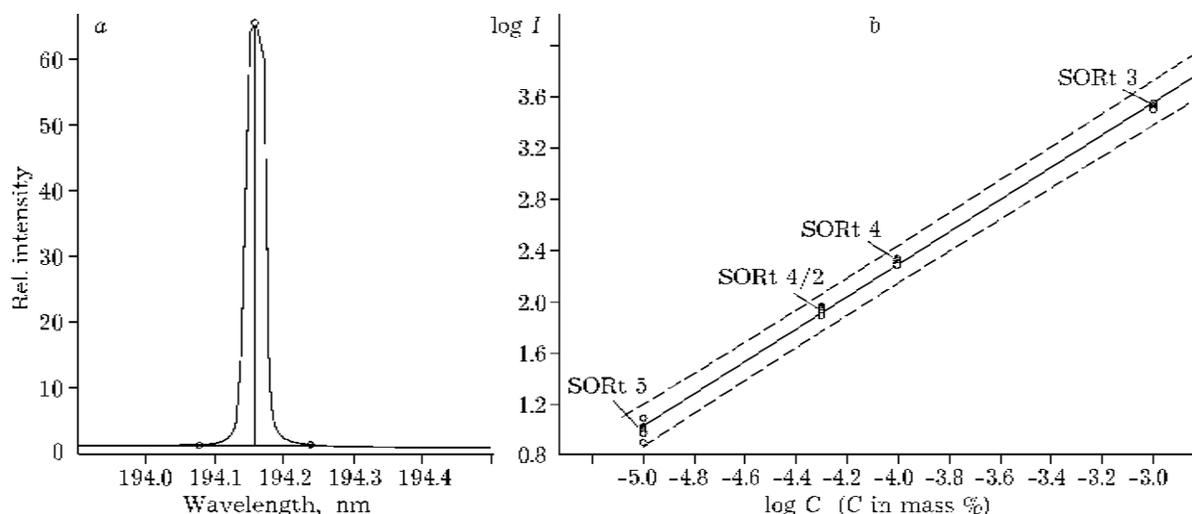

Fig. 3. Contour (*a*) and calibration plot (*b*) of Hg II line 194.164 nm.

TABLE 3

Parameters of calibration plots for the lines of Hg, Na, K, Ca, Li

Element	λ, nm	Calibration plots parameters			Dispersion		Standard calibration plot deviation	Detection limit, 10^{-4} %
					recurrence	accuracy		
		a_0	a_1	α^0	S^2_{rec}	S^2_{ac}		
Hg	II 194.164	2.198	0.61	37.30	0.00147139	0.01005900	0.0112232	3
Hg	I 253.6507	2.139	0.61	43.40	0.00275963	0.05816990	0.0100137	10
Na	I 330.2368	4.548	0.93	43.15	0.00238029	0.00878820	0.0487882	3
K	I 344.672	6.388	0.94	45.51	0.02861330	0.00182908	0.0155400	1
K	I 344.6371	2.431	0.43	43.68	0.00016121	0.00439880	0.0276872	1
K	I 321.702	3.440	0.81	39.08	0.00239009	0.00166252	0.0208220	3
Ca	II 317.9332	3.909	0.64	38.67	0.00289686	0.00113533	0.0163246	3
Ca	II 315.8869	2.852	0.42	43.18	0.00156899	0.00030082	0.0383593	3
Li	I 256.254	2.728	0.54	38.60	0.00110882	0.00077170	0.0318198	3
Li	II 276.6989	4.740	0.96	43.98	0.00465579	0.00844712	0.0231195	3

TABLE 4

Mercury content in CMA-1 samples before regeneration

Sample No. (going up the column)	Content, mass %		Mass in the layer, g	Total mass, g
	AES	AAS		
1	0.32 ± 0.04	0.36 ± 0.05	179.2	
5	0.50 ± 0.06	0.34 ± 0.05	319.2	1120
10	0.70 ± 0.09	0.30 ± 0.04	369.6	2676
15	0.30 ± 0.04	0.50 ± 0.07	672.0	5269
20	0.110 ± 0.014	0.15 ± 0.02	442.4	7991

TABLE 5

Analysis results of n-th column layer with adsorbent CMA-1

Element	λ, nm	Measured, mass %	Number of measurement	Average value, mass %	s_r, %
Li	I 256.254	0.16 ± 0.01	19		
	II 276.6989	0.087 ± 0.013	16		
				0.123 ± 0.034	30
Ca	II 315.8869	0.031 ± 0.006	17		
	II 317. 9332	0.024 ± 0.009	17		
				0.027 ± 0.008	29
K	I 321.702	0.030 ± 0.005	17		
	I 344. 672	0.030 ± 0.002	17		
				0.0300 ± 0.0035	12
Na	I 330.2368	0.032 ± 0.005	17		15

Table 3 for the corresponding calibration plot parameters).

CONCLUSIONS

1. A successful direct atomic emission analysis of mercury and other metals content in powders was demonstrated. A computerized set-up with the arc argon plasma source and diffraction spectrograph with MESA registration was used for the purpose.

2. Methods for analytical signal calculation were checked regarding their influence on the calibration plot parameters and content measurement error. It is proved that using several lines one improves the analysis accuracy. Detection limit C_{min} for mercury by lines is, %: Hg II 194.164 nm − 0.00003, Hg I 253.652 nm − 0.0001, Hg I 312.5665 nm − 0.0025, Hg I 313.184 nm − 0.001. Concentration range for Hg lines is 10^{-5}−2 mass %, *i.e.* five orders of magnitude.

3. Same method provides a simultaneous analysis of content of nuisance admixtures in the mercury containing samples. Typical calibration plots for the used analytical lines are given. Detection limit for admixture elements is $n \cdot 10^{-5}$ mass %.

REFERENCES

1 V. N. Mitkin, L. M. Levchenko, L. A. Khripin *et al.*, Novel Carbon-Containing Demercurisation Sorbents for Ecological Safety in Future Industrial Applications, Proc. of JUPAC CHEMRAWN-IX Congress, Seoul, Korea, 1996, p. 142.

2 Pat. 97115755 USA, 1999.

3 Pat. 2172644 RF, 2001.

4 M. P. Stainton, *Anal. Chem.*, 43, 4 (1971) 625.

5 V. P. Gladyshev, S. A. Levitskaya, L. M. Filippova, Analiticheskaya khimiya rtuti, Nauka, Moscow, 1974.

6 G. Sallsten and K. Nolkrantz, *Analyst*, 123 (1998) 665.

7 N. S. Poluektov, R. A. Vitkun, Yu. V. Zelyukova, *Zh. Anal. Khim.*, 19, 8 (1964) 937.

8 I. M. Koltgof, V. Stender, Obyemny analiz, Goskhimizdat, Moscow−Leningrad, vol. 2, 1952.

9 L. M. Levchenko, V. N. Mitkin, N. N. Komardina, The Mercury Microamounts IVA-Determinations in the Waste Waters and Technological Alkaline Solutions, Abstr. the First Int. Workshop "Siberian Geoanalytical Seminar", Novosibirsk, 1999, pp. 49−50.

10 J. G. Yudelevich, I. R. Shelpakova, S. B. Zayakina and O. I. Scherbakova, *Spectrochim. Acta*, 56 B (1974) 353.

11 A. K. Rusanov, Osnovy kolichestvennogo spektral'nogo analiza rud i mineralov, Nedra, Moscow, 1971.

12 M. L. Shilling, *Zavod. Lab.*, 4 (1956).

13 S. B. Zayakina, G. N. Anoshin, P. A. Gerasimov, *Zh. Anal. Khim.*, 54, 8 (1999) 877.

14 S. B. Zayakina, G. N. Anoshin, *Geostandards Newsletter: J. Geostandards Geoanalysis*, 25, 1 (2001) 57.

15 V. G. Garanin, I. R. Shelpakova, *Spectrochim. Acta*, B56 (2001) 351.

16 S. B. Zayakina, G. N. Anoshin, A. N. Put'makov, V. N. Mitkin, Rasshireniye informativnosti pryamogo spectral'nogo analiza pri ispol'zovanii MAES, Mat. XVI Ural'skoy konf. po spektroskopii (Thesises), Novoural'sk, 2003, pp. 42−43.

17 S. B. Zayakina, A. N. Put'makov, G. N. Anoshin, Rezul'taty modernizatsii difraktsionnogo spektrografa DFS-458S, Mat. V Mezhdunar. simp. "Primeneniye analizatorov MAES v promyshlennosti", Novosibirsk, 2004, pp. 14−24.

18 S. B. Zayakina, Account for the Spatial Parameter Distribution in Two-Jet Plasmatorch Plasma while Analytic Procedures are Developed, in S. B. Zayakina, G. N. Anoshin (Eds.), Proc. XII Int. Conf. on the Methods of Aerophysical Research, part III, Nonparel, Novosibirsk, 2004, pp. 193−197.

19 N. V. Arnautov, N. M. Glukhova, N. A. Yakovleva, Priblizhenny kolichestvenny spektral'ny analiz prirodnykh obyektov, Nauka, Novosibirsk, 1987, p. 73.

20 A. N. Zeidel, V. K. Prokofyev, S. M. Rayskiy, Tablitsy spektral'nykh liniy, Nauka, Moscow, 1977.

21 V. V. Nalimov, Primeneniye matematicheskoy statistiki pri analize veshchestv, Fizmatgiz, Moscow, 1960.

22 A. G. Orlov, Metody rascheta v kolichestvennom spektral'nom analize, Nedra, Leningrad, 1986.

23 Yu. A. Karpov, I. A. Mayorov, L. N. Filimonov, *Zavod. Lab. Diagn. Mat.*, 67, 2 (2001) 52.

24 Predstavleniye rezul'tatov khimicheskogo analiza (rekomendatsii IUPAC 1994). Komissiya po terminologii Nauchnogo soveta RAN po analiticheskoy khimii, *Zh. Anal. Khim.*, 53, 9 (1998) 999.

25 L. M. Levchenko, S. B. Zayakina, V. N. Mitkin *et al.*, Kontrol' soderzhaniya rtuti v promyshlennykh probakh, Mat. V Mezhdunar. nauch.-prakt. konf. "Ekologiya i zhizn'" Penza, 2002, pp. 148−150.

26 L. M. Levchenko, V. N. Mitkin, S. B. Zayakina, T. N. Denisova, Analiticheskiy kontrol' soderzhaniya rtuti v tekhnologii ochistki stochnykh vod, Mat. Vseros. konf. "Aktual'nye problemy analiticheskoy khimii" (Thesises), Moscow, 2002, vol. 2, pp. 133−134.

27 L. M. Levchenko, V. N. Mitkin, S. B. Zayakina, T. N. Denisova, Kontrol' soderzhaniya rtuti v tekhnologicheskikh rastvorakh i otrabotannykh rtut'soderzhashchikh uglerodnykh sorbentakh litiyevogo proizvodstva, Mat. III Mezhdunar. simp. "Kontrol' i reabilitatsiya okruzhayushchey sredy", Tomsk, 2002, p. 110.