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# Technique for implementation of measurements of the metals weight content of in sample of atmospheric aerosol by atomic-emission spectroscopy with a multichannel analyzer of emission spectrum

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## ABSTRACT

The experience of research on the analysis of industrial and atmospheric aerosols by atomic emission spectroscopy is summarized. Various methods of Petryanov filters preparation for spectral analysis have been investigated. It has been shown that for all brands of these aerosol analytical filters, the best at the moment is a combined method of sample preparation. To optimize the conditions of atomic emission analysis, an appropriate carrier was selected. On the basis of the research conducted, a technique for the atomic emission determination of metals in atmospheric air samples, the working area and emissions has been developed.

**Keywords:** atmosphere, chemical composition, elements, heavy metals (HMs), technique, accuracy, trueness, precision.

## 1. INTRODUCTION

Control over the content of heavy metals (HMs) in the atmosphere is a complex analytical task, for the solution of which modern methods of analysis are involved. The most express and universal of them is the method of atomic emission spectroscopy (AES), an important advantage of which is the possibility of simultaneous quantitative determination of a large number of elements in a wide range of concentrations with an acceptable determination bias<sup>1-10</sup>. However, the widespread use of AES for analyzing the atmosphere of urbanized areas is complicated by the lack of reliable, metrologically certified and express methods of analysis.

The aim of this work is to develop a chemical-spectral method for the quantitative determination of a wide range of heavy and toxic metals in ambient air, working area air and industrial emissions. HMs in the air basin are mainly present in the form of solid aerosols, less frequently in gaseous form (mercury). For the extraction of aerosol air particles most often use different filters: from fiberglass, ceramics, Teflon, polyamide, graphite and other materials.

The results of the study of a number of filter materials showed the feasibility of using fine-fiber Petryanov filters (FP), which, even at high filtration rates ( $> 1$  m/s), catch at least 90% of aerosols with a particle size of 0.2  $\mu\text{m}$  and above.

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## 2. METHOD DEVELOPMENT

The means of a one-time control of aerosols developed on the basis of the FP material include analytical aerosol filters (AFA): AFA-KhA (for chemical analysis from acetylcellulose material), AFA-KhS and AFA-RS (for chemical and radioactive analysis from polystyrene), AFA-VP and AFA-KhP (for weight and chemical analysis from perchlorovinyl). Due to the specifics of sampling air aerosols, the metals that are in their composition are associated with the filter material. The technique of direct determination by the method of atomic emission spectroscopy is burdened by large errors, since a strong gassing during the combustion of the organic part of the filter does not ensure the uniform flow of impurities into the discharge. For this reason, preliminary preparation of filter materials for atomic emission analysis, which provides quantitative influx of controlled components from the organic filter matrix to a new collector that meets the requirements of atomic emission spectroscopy, is an integral part of the developed techniques. In the study of atmospheric aerosols, the ash residue obtained after thermal mineralization of the filter in a mixture with a "buffer" is subjected to spectral analysis. Thermal decomposition of the filter material is preferable for spectral analysis, since it involves mineralization of the organic component in a single cycle with obtaining analytical concentrate without additional use of reagents, which helps reduce the level and fluctuations of the blank experiment. However, this method is applicable only to perchlorovinyl-based filters, when ashing occurs, a brittle carbon skeleton is formed. The thermal destruction of the AFA-KhA filters goes through a melt stage, making it difficult to separate the analytical concentrate from the walls of the dish. For the complete decomposition of the organic base of the filters, their ashing was carried out in a stream of oxygen in a quartz tubular micro furnace. To do this, the filter was placed in a tube-container, squeezed it there on the principle of a piston system, the container was introduced into a tube-oven and heated to 250–300 °C, adjusting the temperature using a transformer. Oxygen was supplied metered through a peristaltic pump (Fig. 1). In the analysis of atmospheric aerosols, graphite powder containing 5 % mass. Na in the form of chloride was used as a buffer. Table 1 shows the results of the analysis, which indicate the absence of a systematic bias at the stages of sample preparation and quantification; relative standard deviation of the analysis results ( $S_r$ ) does not exceed 0.20. Thus, the developed methodology can be effectively applied to the analysis of atmospheric air, air of the working zone of enterprises, industrial emissions for the content of heavy and toxic metals, which will improve the environmental safety of urban areas.

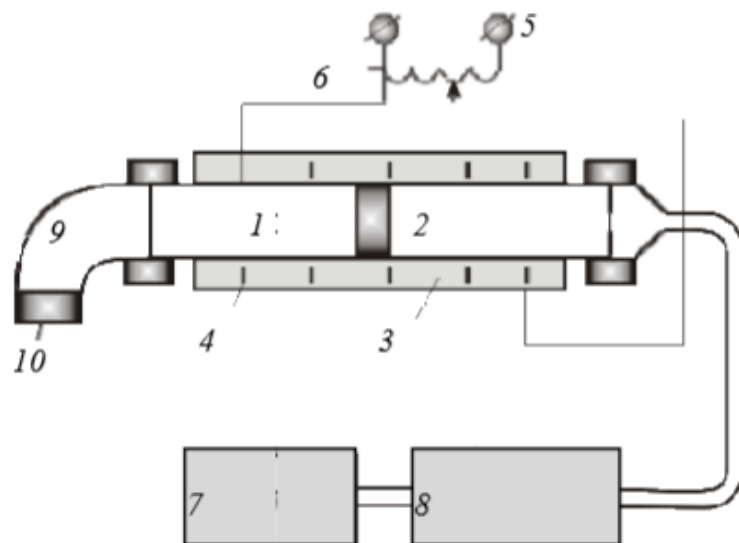


Figure 1. The installation scheme intended for the sample preparation of filters AFA-KhP, AFA-VP by burning them in an oxygen stream: 1 - quartz tube-container; 2 - filter; 3-quartz tube; 4-helix; 5 - AC input from 200 V; 6 - transformer; 7 - tank with oxygen; 8 - peristaltic pump; 9 - absorption cell; 10 - absorber.

Table 1. Verification of the trueness of the analysis technique for the AFA-KhP filters after their mineralization by the combined method ( $n = 5$ ,  $P = 0.95$ ,  $t_{\text{theor}} = 2.78$ )

Element	Permission $\mu\text{g}/\text{filter}$	Found $\mu\text{g}/\text{filter}$	$S_r$	$t_{\text{exp}}$
Ba	1.0	$0.89 \pm 0.21$	0.19	1.45
Be	0.1	$0.098 \pm 0.009$	0.07	0.64
Bi	0.5	$0.47 \pm 0.07$	0.13	1.12
Cd	0.5	$0.45 \pm 0.09$	0.16	1.60
Co	1.0	$0.95 \pm 0.09$	0.08	1.49
Cr	1.0	$0.85 \pm 0.20$	0.19	2.10
Cu	0.1	$0.095 \pm 0.013$	0.12	1.02
Fe	0.5	$0.48 \pm 0.11$	0.19	0.50
Mn	0.1	$0.099 \pm 0.011$	0.09	0.25
Mo	0.1	$0.089 \pm 0.016$	0.15	1.90
Ni	0.5	$0.48 \pm 0.10$	0.17	0.56
Pb	0.5	$0.46 \pm 0.12$	0.20	0.96
Sb	1.0	$0.91 \pm 0.19$	0.16	1.34
Ti	0.5	$0.54 \pm 0.14$	0.20	0.81
V	0.1	$0.092 \pm 0.022$	0.20	1.00
Zn	0.5	$0.47 \pm 0.11$	0.19	0.75

For the results of the air aerosols analysis the bias values are taken equal to: 25% rel. in the whole range of the determined contents of the controlled components in accordance with GOST 12.1.005-88 "General sanitary and hygienic requirements for the air of the working area"; and 50% rel. at the level of the lower boundary of the determined contents (Standard SEV 5557-86. Technical specification). The characteristics of the accuracy of the results for the metal content determination in air samples (atmospheric, working area, emissions) according to the developed technique for the AES method are given in Table 2.

Table 2. Measurement ranges, values of bias characteristics and their components when measuring the weight fraction of metals in samples of atmospheric air, working area air and industrial emissions by the AES method.

Measurement range of weight fraction $X$ , $\mu\text{g}/\text{m}^3$	Reproducibility $\sigma_R$ , $\mu\text{g}/\text{m}^3$	Trueness index $\Delta_c$	Accuracy index $\Delta$ , $\mu\text{g}/\text{m}^3$	Reproducibility limit $R$ , $\mu\text{g}/\text{m}^3$
From 0,1 to 1 inclusive	0,10X	not meaning	0,20X	0,28X
Over 1 to 10 inclusive	0,13X	not meaning	0,25X	0,36X
Over 1 to 100 inclusive	0,15X	not meaning	0,30X	0,42X

When performing measurements of the weight content of metals in air samples in which the content of these elements exceeds  $100 \mu\text{g}/\text{m}^3$ , the determination range is provided by the dilution procedure provided for by the method. The result of the analysis is attributed to the value of the bias characteristic, calculated taking into account the bias established for the range preceding the dilution range.

According to the calibration graphs constructed using standard samples (SO) in the coordinates ( $\lg I - \lg C$ ), find the weight fraction (%) of the determined elements in the blank samples and in the concentrates of air samples. The content of the element being determined in the analyzed air samples ( $C_x$ ,  $\mu\text{g}/\text{m}^3$ ) is calculated by the formula:

$$C_x = \frac{(C_{\text{sample}} - C_{\text{blank}}) \cdot 500}{V}, \quad (1)$$

where  $C_{\text{sample}}$  - the weight fraction of the element to be determined in the concentrate of the analyzed sample, measured on the instrument, % mass;

$C_{\text{blank}}$  - weight fraction of the element to be determined in the concentrate blank, measured on the instrument, % mass;

500 is the translation factor;

$V$  is the volume of air aspirated through the filter,  $V = \nu \cdot \tau$ ,  $\text{m}^3$  ( $\nu$  is aspiration rate or air consumption during sampling,  $\text{m}^3 / \text{min}$ ;  $\tau$  is sampling time,  $\text{min}$ ).

If the measurement were carried out after additional dilution of the sample concentrate with powdered graphite, the content of the element to be determined in the air sample is calculated by the formula:

$$C_x = \eta \frac{(C_{\text{sample}} - C_{\text{blank}}) \cdot 500}{V}, \quad (2)$$

where  $\eta$  is the degree of additional dilution of the sample concentrate.

The measurement results are in the form:  $\bar{X} \pm \Delta$ ,  $\mu\text{g}/\text{m}^3$  ( $P = 0.95$ ),

where  $\bar{X}$  is the arithmetic average value of the two measurement results,

$\pm \Delta$  - limits of the characteristics of the bias of measurement results for a given weight fraction of the element being determined (Table 1),  $\mu\text{g}/\text{m}^3$ .

The developed method is designed to determine: Al, Ag, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Si, Sn, Sr, Ti, V, Zn, Zr by the method of arc atomic emission spectroscopy (AES) using a multichannel analyzer of emission spectra (MAES) in laboratories that have equipment for analyzing with this method. The technique provides a determination of the weight content of the elements to be determined at the level of maximum one-time maximum permissible concentrations of elements for atmospheric air (RD 52.04.186-89) and working area air (GOST 12.1.005-88) with a minimum volume of the analyzed air equal to  $0.02 \text{ m}^3$  for copper, lead and  $0.01 \text{ m}^3$  - for the remaining elements. The recommended volume of air sample for analysis is  $0.05 \dots 0.1 \text{ m}^3$ . The technique was developed using a complex of atomic emission spectral analysis combined with a MAES analyzer. The complex includes a multichannel spectrometer "Grand" (calibration certificate No. 55586/203 from 07.11.2018, valid until 07.11.2019), a spectroanalytical generator with electronic control "Vesuviy-3", providing five types of discharge (direct current arc, intermittent current arc, alternating current arc, combined discharge and spark discharge). To register the spectra with the help of MAES, the conditions providing the highest sensitivity of the determinations are used: current 13 A; slot width 30 microns; distance between electrodes 0.003 m; aperture of 0.005 m; accumulations -160; accumulation duration is 125 ms; full exposure at registration of the spectra of the analyzed samples and control samples 20 s. For the construction of calibration graphs were used standard samples of the composition of the graphite collector of trace contaminants set SOG-37. Also it may be used similar sets of state standard samples, providing the calibration of the controlled elements: a set of SOG-21, a set of SOG-28. Lifetime of standards is 60 years.

### 3. QUALITY CONTROL OF RESULTS

The quality control of measurement results when performing the procedure in laboratories includes: operational control of the measurement procedure (based on the evaluation of repeatability and bias in the implementation of a single control procedure); monitoring the stability of measurement results (based on monitoring the stability of the standard deviation of repeatability, interlaboratory precision, bias).

Table 3. Measurement range, values of repeatability, reproducibility and accuracy with a confidence level of  $P = 0.95$ .

Content measurement range - $X$ , $\mu\text{g}/\text{m}^3$ .	Reproducibility limit $R$ , $\mu\text{g}/\text{m}^3$
From 0.1 to 1 inclusive	0.28X
Over 1 to 10 inclusive	0.36X
Over 1 to 100 inclusive	0.42X

The algorithm of the operative control of the measurement procedure using the control sample is carried out by comparing the results of a single control procedure  $K_k$  with the control standard  $K$ . The result of the control procedure  $K_k$  ( $\mu\text{g}/\text{m}^3$ ) is calculated by the formula:

$$K_k = \left| \bar{X} - C \right| \quad (3)$$

where  $\bar{X}$  is the result of the control measurement of the content of the element to be determined in the sample for control,  $\mu\text{g}/\text{m}^3$ ;

$C$  is certified value of the sample for control,  $\mu\text{g}/\text{m}^3$ .

If the result of the control procedure satisfies the condition

$$\left| K_k \right| \leq K, \quad (4)$$

then the analysis procedure is considered satisfactory.

If this condition is not fulfilled, the control procedure is repeated. In case of repeated non-fulfillment, find out the reasons leading to unsatisfactory results, and take measures to eliminate them.

Checking the acceptability of the results obtained under the conditions of reproducibility: the discrepancy between the results of measurements obtained in two laboratories should not exceed the limit of reproducibility. If this condition is fulfilled, both measurement results are acceptable and their overall average value can be used as the final

$$R_k = \left| \bar{X}_1 - \bar{X}_2 \right| \leq R, \quad (5)$$

where  $R$  is values of the limits of reproducibility, are given in table 3.

In case of exceeding the limit of reproducibility, methods can be used to assess the acceptability of measurement results according to section 5 of ISO 5725-6:1994(en) Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values.

## 4. CONCLUSION

Thus, as a result of the research, a method has been created for measuring the weight fraction of metals in samples of atmospheric air, the working area air and emissions by arc atomic emission spectroscopy with a multichannel analyzer of emission spectra. The technique has been tested and prepared for metrological examination.

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## REFERENCES

- [1] Otmakhov, V. I., "Methodological features of creation of atomic-emission techniques for various objects," *Analitika i kontrol* 9 (3), 245-249 (2005).
- [2] Otmakhov, V. I., Rabtsevich, E. S., Babenkov, D. E. and Petrova, E. V., "Development of spectral techniques for the analysis of biological objects of animal origin," *Tomsk State University. Journal of Chemistry* 12, 37–45 (2018).

- [3] Otmakhov, V. I., Varlamova, N. V. and Petrova, E. V., "Structural-Methodological Scheme of Developing the Methods for Analysis of Oxide Materials Using Atomic-Emission Spectroscopy," *Zavodskaya laboratoriya. Diagnostika materialov* 74 (8), 15–17 (2008).
- [4] Babenkov, D. E., Otmakhov, V. I., Petrova, E. V., Poves'ma, Yu. A. and Salosina, Yu. E., "Methodology of selecting the algorithms for optimization of arc spectral analysis," *Zavodskaya laboratoriya. Diagnostika materialov* 85 (1, II), 77-81 (2019).
- [5] Otmakhov, V. I., Kuskova, I. S., Petrova, E. V., Rabchevich, E. S., Kataeva, N. G. and Shilova, I. V., "New Method of Spectral Analysis of Human Hair," *AIP Conf. Proc.* 1772 (050002), 1-8 (2016).
- [6] Otmahov, V. I., "Methods for evaluation the environmental safety of a water basin due to pollution of bottom sediments," *Izvestia TPU* 306 (6), 39–41 (2003).
- [7] Otmakhov, V. I., Sarkisov, Yu. S., Pavlova, A. N. and Obukhova, A. V., "Periodic dependences in the distribution of chemical elements in the human hair ash residue," *Zavodskaya laboratoriya. Diagnostika materialov* 85 (1, II), 73-77 (2019).
- [8] Shilova, I. V., Suslov, N. I., Otmahov, V. I., Zibareva, L. N., Samylina, I. A., Mazin, E. V., Petrova, E. V., Babushkina, M. S., Kovaleva, T. I., Kuskova, I. S. and Krapivin, A. V., "Chemical and pharmacological study of herbal preparations that improve cognitive-mnestic functions," *Pharmaceutical Chemistry Journal* 50 (10), 654-658 (2017).
- [9] Otmakhov, V. I. and Petrova E. V., "Atomic-emissive analysis of biological objects with the purpose of conducting ecomonitoring of Tomsk oblast and Gorny Altay regions," *Izvestia TPU* 307 (1), 73–77 (2004).
- [10] Otmakhov, V. I., Petrova, E. V., Lapova, T. V. and Gindullina, T. M., "Extraction of metal ions from aqueous solutions by polycarbonate microfiber sorbent," *Yale Journal of Science and Education* 16 (1), 469-476 (2015).