Original article

Determining Potassium Bromate in the Inhalable Aerosol Fraction in Workplace Air with Ion Chromatography

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A B S T R A C T

Background: The article presents the results of studies performed in order to develop a new method of airborne potassium bromate(V) determination at workplaces.
Methods: The method is based on a collection of the inhalable fraction of potassium bromate(V) using the IOM Sampler, then extraction of bromates with deionized water and chromatographic analysis of the obtained solution. The analysis was performed using ion chromatography with conductometric detection. The tests were performed on a Dionex IonPac®AS22 analytic column (250×4 mm, 6 μm) with AG22 precolumn (50×4 mm 11 μm).
Results: The method provides for potassium bromate(V) determination within the concentration range of $0.043 \div 0.88$ mg/m^3 for an air sample of 0.72 m^3 in volume, i.e., $0.1-2$ times the exposure limit value as proposed in Poland. The method was validated in accordance with PN-EN 482. The obtained validation data are as follows: measuring range: $3.1-63.4$ μg/mL, limit of detection (LOD) = 0.018 μg/mL and limit of quantification (LOQ) = 0.053 μg/mL. The developed method has been tested in the work environment, on laboratory employees having contact with potassium bromate(V).
Conclusion: The analytical method allowed the determination of the inhalable fraction of airborne potassium bromate(V) at workplaces and can be used to assess occupational exposure.

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1. Introduction

Potassium bromate(V) (KBrO$_3$, CAS no. 7758-01-2) is a substance with no occurrence in the natural environment. It dissolves well in water, dissociating into BrO$_3^-$ and K$^+$ ions. Strong oxidizing properties of potassium bromate(V) were the reason that stood behind using it as a food additive e.g., to flour as a whitening and maturing accelerating agent, to the beer during the malting process, and as an additive used in the production of some types of cheese [1—3] and to cosmetics (as a component of liquid cold-wave lotion) [4]. In 1992, potassium bromate(V) was prohibited from usage as a flour additive by a team of FAO/WHO experts [5]. Potassium bromate(V) is also used in the pyrotechnic industry for fireworks manufacturing, especially crackers [4,6]. It is widely used in analytical chemistry as an oxidizing and brominating agent [7,8].

Bromate ions can also be found in drinking water as a result of secondary pollution of tap water. The presence of bromates in treated drinking water is associated primarily with the ozone reacting with bromide ions, which are naturally present in all types of water, as well as with the presence of bromates as an impurity of hypochlorites used to disinfect water [9—16].

Potassium bromate(V) was classified by the International Agency for Research on Cancer (IARC) as a group 2B substance, that is as an agent that is likely to be carcinogenic to humans [17]. In the European Union, potassium bromate(V) was classified as a class 1B carcinogenic substance, i.e., substances that are presumed to have a potential carcinogenic effect on humans and evidence of carcinogenicity is based on animal studies [18—21]. The toxicity of potassium bromate(V) comes from the bromate anion found in toxicology studies.

The guidelines of the World Health Organization [19] and EU directive [22] for drinking water recommend a BrO$_3^-$ ions threshold value of 0.01 μg/mL as the maximum allowable concentration in drinking water. This is the reason behind the bromate content being reported in various types of water, as well as methods for reducing the bromate content in water [23—27].

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Due to the negligible value of vapor pressure, no release of gaseous potassium bromate(V) into the air is expected, but rather a presence of small amounts of bromate in the form of a particulate aerosol may occur [28]. Hara et al. [29], using ion chromatography, have determined a small amount of bromate presence in the arctic air particles. Bromate concentrations varied from below the detection level $<1.3 \times 10^{-6}$ mg/m^3 up to 24.3×10^{-6} mg/m^3 [29].

Occupational exposure to potassium bromate(V) primarily concerns laboratory employees who work with this substance as an analytical reference or as a reagent.

In order to obtain information necessary for the 2017−2019 project, data on the exposure of workers in Poland to potassium bromate(V) was extracted from the Central Data Registry on Exposure to Substances, Factors, and Technological Processes on Carcinogenic or Mutagenic Effects (IMP, Łódź). These data indicate that during the years 2005−2016, the number of persons exposed to potassium bromate(V) in Poland has increased. In 2016, an increase in both the number of workplaces reporting this factor and an increase in the number of persons exposed compared to 2015 was noted. The number of plants reported in 2016 was 79 and was larger compared to the previous year by 12 plants, while the number of persons exposed for the first time exceeded one thousand and amounted to 1,160 (compared to 687 in 2015) [30]. In Poland, potassium bromate(V) was used mainly in laboratory positions in physiochemical, microbiological, quality control, and research-and-development laboratories, and only 30 of the reported exposed persons were employed in the apparatus operating position in one of the chemical production plants.

Potassium bromate could be carcinogenic for humans, and exposure should be as limited as possible. There are no established limit values in the world for airborne potassium bromate(V) at the workplace. In 2018 in Poland, at the meeting of the Expert Group on Chemical Factors of the *Interdepartmental Commission on Maximum Permissible Concentrations and Intensity of Health Hazardous Factors in the Work Environment,* the value of 0.44 mg/m^3 was proposed as the maximum allowable concentration (MAC) for the inhalable fraction of potassium bromate(V) [30]. The MAC value is effective from 2019 onwards. For the maximum allowable concentration value, the risk of developing kidney cancer at the level of 0.22% and thyroid at the level of 0.06% was calculated. It is apparent that there exists a need to develop a method for determining KBrO$_3$ in the range of 0.1−2 times the allowable concentration in air, i.e., from 0.044 to 0.88 mg/m^3.

Articles describing the methods of determination of potassium bromate(V) can be found in the literature, mostly in samples of bread and flour [3,31−34], as well as in water (e.g., in swimming pool, potable) [13,15,20,23,35]. The main methods utilized for this purpose are spectrophotometry [3,31,32] and chromatographic methods − the ion chromatography primarily [14,15,25,36,37]. Spectrophotometric and electrochemical methods are most commonly used to determine inorganic anions in environmental samples. Especially in terms of selectivity and sensitivity, ion chromatography is a competitive technique for these instrumental techniques [6,35,38,39]. Institutions controlling water quality for the analysis of bromate content in drinking water use analytical methods based on ion chromatography with various detection techniques [40−43].

Each of the proposed methods requires a selection of optimum chromatographic conditions as necessary in order to obtain correct separation of the substances analyzed, as well as a determination of their concentration, as only in this manner will it be possible to obtain reliable results, in particular in the very low concentrations range. In order to determine potassium bromate(V) in the aerosol's inhalable fraction in the work environment, ion chromatography with conductivity detection was selected and used as a sensitive,

accurate, as well as repeatable method, widely used for direct determination of various types of inorganic ions [14,15,37,43].

Taking air samples is an essential step for determining the content of harmful substances in the air.

This paper presents a new methodology of potassium bromate(V) determination in workplace air, meeting the specified requirements for the procedures for the measurement of chemical agents [44] and legal requirements in Poland.

2. Materials and methods

2.1. Apparatus, reagents, and materials

The following equipment was used in the studies: Dionex ICS-500 ion chromatograph equipped with Dionex AS-AP autosampler, ASRS 300 (4 mm) suppressor, and conductivity detector of Thermo Scientific brand (USA).

The test was performed using a Dionex IonPac®AS22 analytic column (250 × 4 mm, 6 μm) with AG22 protective column (50 × 4 mm, 11 μm), suitable for the determination of low molecular weight inorganic anions and organic acids. The suitable pH range for the column is 0 ÷ 14.

The following equipment was used for sample collection: the IOM-type Inhalable Samplers (IOM sampler) made by SKC Inc (USA), filters made of a mixture of cellulose esters (MCE), 0.8 μm of 25 mm diameter by SKC (USA), glass fiber filters (GF/A) of 25 mm diameter by Whatman (UK), Teflon filters (PTFE) of 25 mm diameter by SKC (USA) and GilAir PLUS Personal Air Sampling Pump by Sensidyne, (USA).

Also the following reagents and materials were used: inorganic anion reference solution Dionex™ Combined Seven Anion Standard II containing: F$^-$ (20 μg/mL), Cl$^-$ (100 μg/mL), NO$_2^-$ (100 μg/mL), Br$^-$ (100 μg/mL), NO$_3^-$ (100 μg/mL), PO$_4^{3-}$ (200 μg/mL), SO$_4^{2-}$ (100 μg/mL) by Thermo Scientific (USA), potassium bromate(V) by Merck (USA), potassium bromate(V) reference solution of c = 1000 μg/mL ± 4 μg/mL by Sigma-Aldrich (Switzerland), ammonium acetate by Merck (Germany). Sodium bicarbonate and sodium carbonate mixture (NaHCO$_3$/Na$_2$CO$_3$) prepared using a Dionex AS Eluent Concentrate NaHCO$_3$/Na2CO$_3$ (4.5 mM/1.4 mM) standard by Thermo Scientific (USA) was used as the carrier phase for the analysis of bromate ions.

Calibration solutions were made by diluting commercially available reagents: potassium bromate(V) or potassium bromate(V) reference solutions having a concentration of 1000 μg/mL and ammonium acetate with deionized water obtained from the Elix 3 system (Millipore, USA).

Until the analysis, the samples were stored in polyethylene vessels at 5 °C until IC analysis was performed.

2.2. Method validation

Based on the required criteria for the optimal validation scope of research methods used in analytical chemistry, the following were determined: precision, linearity, accuracy, quantification, sensitivity, and measurement uncertainty [44]. The statistical hypotheses were tested and verified using Snedecor's F and Student *t* tests.

2.3. Method of collecting air samples

In order to collect the inhalable fraction of potassium bromate(V) from the air, a system consisting of a battery-powered pump was used, which induces an airflow of 2 liters per minute through a filter placed in the IOM-type Inhalable Sampler. The whole system is placed on an employee (probe to be located in the breathing

zone) and is used to simulate how air is inhaled through the nose and mouth.

3. Results and discussion

3.1. Determining the operating conditions of ion chromatography system with conductivity detection

The optimal operating parameters of the ion chromatograph determined based on the tests are presented in Table 1.

Under these conditions, it was possible to separate bromate ions from other co-occurring ions. Fig. 1 shows the chromatogram of the anion standard solution obtained under the indicated operating conditions of the ion chromatograph (fluorides c = 2 μg/mL, acetates c = 10 μg/mL, bromates(V) c = 10 μg/mL, chlorides c = 10 μg/mL, nitrates(III) c = 10 μg/mL, bromides c = 10 μg/mL, nitrates(V) c = 10 μg/mL, phosphates(V) c = 20 μg/mL, sulfates(VI) c = 10 μg/mL).

The separation conditions have been selected so that the potentially interfering anions do not affect the determination of bromates (V). Resolution of bromate(V) peak and the other closest peak that is chloride peak was above 1.55 (calculations were performed for a reference solution containing 32 μg/mL each of bromates(V), whereas chloride ion level was varied throughout the concentration range of 10 ÷ 750 μg/mL). The resolution values obtained conformed to the requirements set out by the PN-EN ISO 15061 standard [43]. The results indicate that the chloride content (up to 750 μg/mL) will not impact the bromate signal reading.

3.2. Determination of air sample collecting conditions for the determination of potassium bromate(V) in the inhalable fraction of an aerosol

3.2.1. Examination of recovery of bromate from filters

In order to determine the air sample collection conditions for the determination of potassium bromate(V), an IOM sampler was used to isolate the inhalable fraction. The GilAir PLUS pump suitable for allowing air through the probe with a stable flow of 2 L/min was used to collect the appropriate volume of air, i.e., to collect up to 0.72 m^3 of air within 6 hours. The suitability of three types of filters for use in the IOM sampler has been tested.

The recovery test was carried out for materials used in samplers to isolate the aerosol fraction from the air. Thus, the recovery of bromate from glass fiber filters and filters from a mixture of cellulose esters (MCE) and PTFE filters was assessed.

A Milli Q deionized water was used to extract the BrO$_3^-$ ions from the filter media.

Suitability of filters for collection of an inhalable fraction of aerosol: GF/A Filter (glass fiber filters), MCE Filter (filters made of cellulose ester mixture), Teflon Filter (PTFE filters) were examined as follows: twelve filters were prepared − four of each type, filter

surface was dripped onto with 0.1 mL of bromate stock solution of c = 984 μg/mL and left for about 1 hour to dry. At this stage, a PTFE filter has been eliminated, as its structure prevented absorbing the applied solution.

Two MCE filters and two GF/A filters were placed in IOM samplers, which were then connected with pumps forcing the airflow with a stable flow of 2 L/min (as required for IOM samplers) for 3 hours. Based on preliminary tests, it was found that shortening the air permeation time from 6 to 3 hours during the filter differentiation test does not affect the results. A 6-hour sampling time was used to determine the validation parameters.

The filters were individually taken and placed in closed containers, 10 mL each of water was added and was shaken for 30 minutes in a shaker. A reference solution of potassium bromate(V) prepared using 0.1 mL of c = 984 μg/mL potassium bromate(V) solution with 10 mL of water was analyzed. The comparison of results is shown in Table 2.

When checking the blank samples, the presence of chloride and fluoride ions was found, which are eluted by water from clean GF/A (F$^-$ and Cl$^-$) and MCE (Cl$^-$) filters during shaking.

The results presented in Table 2 show that for the GF/A filters, slightly larger bromate recovery values were obtained (105.2%) than for MCE filters (102.1%). The GF/A filters were nevertheless not used in further studies. High chloride concentration in these filters could influence the correct reading of bromate peaks area. Moreover, these filters are destroyed during a half-hour shaking cycle (are separated into smaller fragments), which could result in a lack of repeatability of results. MCE filters were thus selected for collecting air samples.

3.2.2. Verification of the proposed method of collecting air samples

In order to determine the inhalable fraction of airborne potassium bromate(V) dust, the use of a probe was proposed − an IOM sampler (suitable for collecting an inhalable fraction of airborne dust) equipped with an MCE filter (as an absorbent material) connected to a pump that forces the air through the sampling head with a volumetric airflow of 2 L/min (as dedicated for the IOM sampling head). The suitability of the adopted method of sampling was checked in the following manner: a potassium bromate(V) reference standard was poured onto a weighing dish, and the air from above the standard was absorbed (standard provided as fine powder − approx. 3 mg). An IOM sampler for collecting the inhalable fraction of dust with the installed MCE filter (diameter of 25 mm) was connected to the filter holder having a diameter of 25 mm (the reference MCE filter was also placed in the holder), and the air was passed for half an hour through such prepared set (in the meantime, the KBrO$_3$ powder was added and mixed).

Chromatograms obtained after filter extraction with water showed potassium bromate(V) retention on a first filter (used in IOM sampler). Also, on the chromatograms, there were no peaks corresponding to bromates from solutions obtained from shaking

Table 1
Ion chromatograph operating conditions

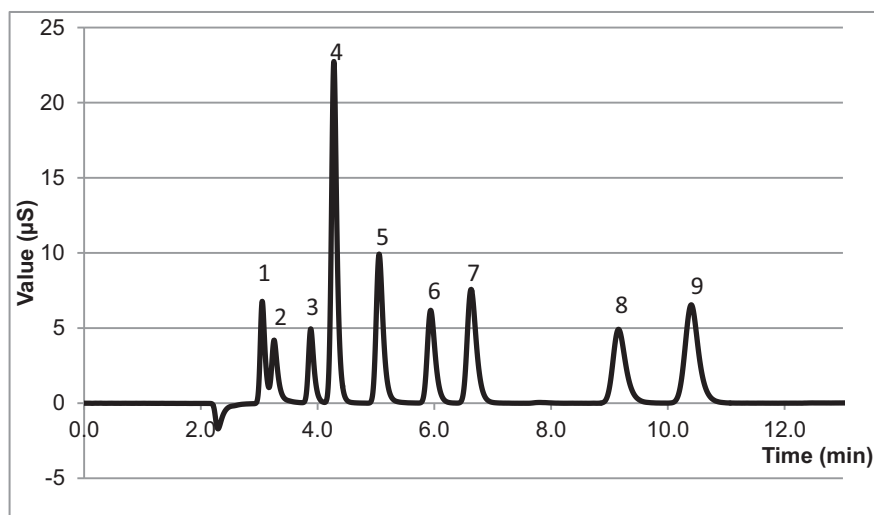| Chromatograph parameters	Determined conditions
Eluent	4.5 mM NaHCO$_3$/1.4 mM Na$_2$CO$_3$
Mobile phase flow rate	isocratic: 1.2 mL/min
Column temperature	30 °C
Detector	Conductivity detector
Column	Anionic column Ion-PacAS22 (250 × 4 mm) with precolumn AG22 (50 × 4 mm)
Suppressor	Dionex ASRS 300 (4 mm)
Current	31 mA
Injection volume	50 μL

Fig. 1. Chromatogram of Dionex Seven Anion Standard II reference solution of inorganic anions: (1) fluorides, (4) chlorides, (5) nitrates(III), (6) bromides, (7) nitrates(V), (8) phosphates(V), (9) sulfates(VI) combined with (3) potassium bromate(V) solution and (2)ammonium acetate solution.

of control filters, which indicated that effective absorption of bromates could be assured by a single filter. The presence of bromates in the air above the solid substance, which was poured and mixed by the laboratory technician, was confirmed.

3.2.3. Stability of samples

The stability of the collected air samples depending on the storage time was tested as follows: 0.05 mL of a solution of $KBrO_3$ 4.14×10^3 μg/mL was spotted on MCE filters. After water evaporation, the filters containing 207 μg potassium bromate(V) were placed in plastic containers and stored in a desiccator. The stability of MCE filters with absorbed potassium bromate(V) was assessed during storage for 7 days. After this time, the filter was shaken for half an hour with 10 mL of water, and the obtained solution was subjected to ion chromatography analysis with conductivity detection. Each analysis was carried out in three parallel replicates. For filters stored in the desiccator and analyzed after 1, 2, 3, 6, and 7 days the change in peak area [%] was calculated and compared with the results obtained on the day of sample preparation. The results are presented in Table 3.

The obtained results were within ±5% below the average value, which proves that samples remained stable during the examined period. Potassium bromate(V) absorbed in the MCE filter remains stable for 7 days when stored in a desiccator.

3.3. Determining the measuring range and calibration tests

It is assumed that the measurement procedure used for assessing employee occupational exposure should allow determination of the substance in the range of 0.1−2 times the value of the maximum permissible concentration [44]. The MAC value for potassium bromate(V) in Poland was established at the level of 0.44 mg/m³ [30]. This value was recalculated into the absorption of potassium bromate(V) from the air (with airflow of 2 L/min) during a 6-hour (360 min) period, i.e., an air sample of 0.72 m³ in volume, and during recovery, a dilution was taken into account (recovery using 10 mL of water). Therefore, three series of standard solutions of potassium bromate(V) in the concentration range 3.1−63.4 μg/mL were prepared for calibration tests.

The calibration solutions prepared were subjected to chromatographic determination. Then a calibration curve was plotted, with potassium bromate(V) concentration in micrograms per milliliter on the abscissa and the corresponding average peak areas on the ordinate (Fig. 2).

In the tested range of concentrations, an unsatisfactory correlation coefficient of 0.9982 was obtained for a linear fit, while the match of calibration points to a second-degree polynomial function, the correlation coefficient found was 0.9999. PN-ISO 8466-2 [45] (concerning water quality testing) recommends that the relationship between a set of calibration points is defined using a second-degree polynomial if it is not possible to apply linear regression analysis.

For the plotted calibration curves of potassium bromate(V) as a linear and polynomial function, a residue analysis was performed, which proved the match of the calibration points to the polynomial

Table 2
Results of KBrO₃ absorption and recovery using various filters

	Sample no.	Peak area from 1. injection	Peak area from 2. injection	Average area of peaks	Average recovery, %
Reference solution	1	0.4471	0.4382	0.4451	—
	2	0.4475	0.4474		
Solution after shaking of MCE filter	1	0.4325	0.4442	0.4415	99.2%
	2	0.4441	0.4450		
Solution after shaking of MCE filter (through which air was passed)	1	0.4573	0.4596	0.4543	102.1%
	2	0.4493	0.4509		
Solution after shaking of GF/A filter	1	0.5412	0.5330	0.4954	111.2%
	2	0.4523	0.4551		
Solution after shaking of GF/A filter (through which air was passed)	1	0.4721	0.4736	0.4682	105.2%
	2	0.4628	0.4643		

Table 3
Results of stability testing of MCE filters with KBrO₃ absorbed, stored in a desiccator

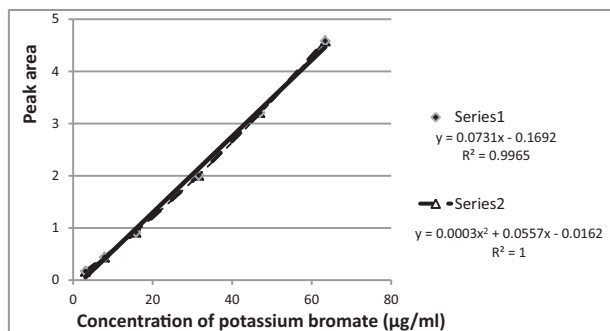| Storage time [number of days]	Average area of peaks	Standard deviation	Change in peak area [%] after sample storage
0	0.895	0.012	—
1	0.885	0.006	-1.15
2	0.911	0.013	1.77
3	0.880	0.037	-1.68
6	0.918	0.049	2.53
7	0.925	0.037	3.29

Fig. 2. Graph of the potassium bromate(V) calibration curve as a linear function (series 1) and second-degree polynomial function (series 2).

function was correct and to the model of the linear function was incorrect.

A homogeneity test of the variance of the determined calibration range was also carried out, and verification was made on whether the variances of the measured values obtained for the selected standard solutions are uniform and independent of the concentration (made at the significance level $\alpha = 0.05$). According to the results of the Snedecor F test, the F_{calc} value referring to the range of calibration points was 3025 and was larger than the critical value (derived from the tables) F_{crit} ($n_1 = n_2 = 4$; $\alpha = 0.05$) = 6.39, therefore, the difference between variances was significant. The entire range of the calibration curve does not meet the requirements of the Snedecor F test, which would allow defining all calibration points using a linear relationship, and in such case, the match of calibration points using a second-degree polynomial function shall be used.

From the results of three series of $KBrO_3$ standard solutions in the concentration range 3.1–63.4 µg/mL, standard deviations and coefficients of variation were calculated. The coefficients of variation for the subsequent concentration levels were respectively: 0.68%, 3.42%, 2.32%, 1.84%, 2.05%, and 1.54%. The mean coefficient of variation (1.97%) was included in the relative uncertainty of the analytical process.

3.4. Precision testing

In order to determine the precision of the analytical part, three series of standard solutions of bromate ions (BrO_3^-) were prepared, with the concentration of 3.55, 10.38, and 51.90 µg/mL respectively, 8 solutions each. Then each of the solutions was subjected to chromatographic analysis.

Based on the measured peak areas, the standard deviation and the coefficient of variation for a given concentration level were calculated. Then the average precision was determined as the average coefficient of variation for the range of concentrations (Table 4).

As the total precision of the method, the mean coefficient of variation, with the value of 5.56%, was adopted.

3.5. Recovery test for three concentrations within the measuring range

In order to confirm the correctness of the selected air sampling conditions, the recovery efficiency of potassium bromate(V) from filters from a mixture of cellulose esters was determined for three concentrations within the measuring range. For this purpose, 0.025 mL each of 1.42×10^3 µg/mL, 4.14×10^3 µg/mL and 20.7×10^3 µg/mL $KBrO_3$ solution in water was applied to MCE

filters. The results were respectively 35.5 µg, 103.5 µg, and 517.5 µg potassium bromate in the samples.

Six samples per each level of concentration were prepared. After drying out, each filter was placed in an IOM sampler, which was then connected to a pump and run for 6 hours. The airflow was 2 L/min. In the next step, the filters were shaken for half an hour in 10 mL of water, and the resulting bromate solutions were injected into the apparatus in order to perform chromatographic analysis. For each series, three reference solutions were also prepared with the following concentrations: 3.55; 10.35, and 51.75 µg/mL, respectively. These solutions were also subjected to chromatographic analysis.

The results of the recovery tests are presented in Table 5. The average recovery for $KBrO_3$ was 99%.

3.6. Validation parameters of the developed method

Validation of this method was performed in accordance with the requirements specified in the PN-EN 482 standard [44]. The method was validated while also establishing parameters such as measuring range, precision, recovery rate, detection, and quantification limit, as well as total and extended uncertainty.

For calculating the standard deviation (s_o) of the data results obtained for a series of blank samples, 10 independent peak area measurements were carried out with retention time of the analyte tested for three independently prepared blank samples, which were obtained by extraction from the MCE filter used for sample collection using 10 milliliters of deionized water. During the retention, the noise level corresponding to BrO_3^- ions, i.e., 3.7–4.15 min was determined. Calculated LOD and LOQ values were LOD = $x_{avg} + 3 \cdot s_o$ and LOQ = $3 \cdot$LOD.

Possible sources of uncertainty for the measurement of the substance in the working environment have been identified, and components, including sampling and laboratory testing expressed as relative standard uncertainties in percent (u), have been included.

The set of uncertainty factors includes significant components, i.e., uncertainty associated with the pump flow stability, the uncertainty of flow rate and time measurements, the uncertainty of the calibration, uncertainty of analytical precision, and uncertainty related to recovery.

The total relative uncertainty (uc) was calculated as the sum of all identified components of the relative uncertainties of the sampling and analytical steps, which were expressed as percentages, using the formula (1):

$$u_c = \sqrt{u_1^2 + u_2^2 + \dots + u_n^2} \tag{1}$$

The expanded uncertainty U, expressed as a percentage, using a coverage factor k = 2 for a 95% confidence level, was calculated according to formula (2):

$$U = k \cdot u_c \tag{2}$$

Table 6 shows the validation data of the determination method of potassium bromate(V), obtained based on the results of the tests.

3.7. Studies at workplaces

The developed method has also been tested in the work environment, on laboratory employees having contact with potassium bromate(V). Measurements of the concentration of $KBrO_3$ in the air were carried out at the stations where these substances were used as follows: potassium bromate with potassium bromide as a titrant when determining mercury in water samples using fluorescence

Table 4
Precision parameters for three measurement series of differing KBrO$_3$ concentration

Series 1		Series 2		Series 3	
3.55 µg/mL KBrO$_3$ solution		10.38 µg/mL KBrO$_3$ solution		51.84 µg/mL KBrO$_3$ solution	
Average area of peak	0.1829	Average area of peak	0.4538	Average area of peak	2.654
Standard deviation	0.0055	Standard deviation	0.0089	Standard deviation	0.058
Coefficient of variation ν_1 [%]	3.01	Coefficient of variation ν_2 [%]	1.96	Coefficient of variation ν_3 [%]	2.19
Mean precision — average coefficient of variation for the range [%]					2.43
Total precision of the test — average coefficient of variation [%]					5.56

spectrophotometry or chlorprothixene in the medicinal product (potentiometric titration) and for the potassium bromate standard, from which calibration solutions to be used for determining bromate content water samples by ion chromatography were prepared using potassium bromate standard.

Air samples at workplaces were collected using individual dosimetry in accordance with the Polish Standard PN-Z-04008-7

[46]. The sampler used to collect the inhalable fraction was placed together with the MCE filter (made of a mixture of cellulose esters) in the sampler, and was in each case, attached in the employee's breathing zone, and the pump connected to the sampler was hung on the belt so as not to restrict the employee's movement. The air sample collection time was 6 hours (constant airflow rate through the sampler of 2 L/min).

Table 5
Determination of KBrO$_3$ recovery from the MCE filter

Area of peaks in recovery solutions	Average area of peaks in recovery solutions	Average area of peaks in comparative solutions	Recovery	Average recovery [%]
35.5 µg KBrO$_3$ applied onto the filter				
1 0.1813 0.1774	0.1794	0.182 ± 0.005	0.99	100.2
2 0.1682 0.1803	0.1743		0.96	
3 0.1828 0.1836	0.1832		1.01	
4 0.1838 0.1852	0.1845		1.02	
5 0.1869 0.1857	0.1863		1.03	
6 0.1833 0.1839	0.1836		1.01	
Average area of peaks in recovery solutions				0.180
Standard deviation				0.005
Relative standard deviation [%]				2.78
103.5 µg KBrO$_3$ applied onto the filter				
1 0.4521 0.4499	0.4500	0.472 ± 0.008	0.95	97.1
2 0.4616 0.4656	0.4600		0.97	
3 0.4574 0.4675	0.4600		0.97	
4 0.4480 0.4692	0.4600		0.97	
5 0.4666 0.4651	0.4700		1.00	
6 0.4516 0.4556	0.4500		0.95	
Average area of peaks in recovery solutions				0.460
Standard deviation				0.010
Relative standard deviation [%]				2.17
517.5 µg KBrO$_3$ applied onto the filter				
1 2.64 2.64	2.64	2.56 ± 0.005	1.03	101.0
2 2.68 2.70	2.69		1.05	
3 2.52 2.37	2.45		0.96	
4 2.62 2.66	2.64		1.03	
5 2.41 2.56	2.49		0.97	
6 2.52 2.58	2.55		1.00	
Average area of peaks in recovery solutions				2.58
Standard deviation				0.10
Relative standard deviation [%]				3.88

Table 6
Validation data for the determination method of potassium bromate(V)

Parameter	Determined value of the parameter
Measurement range	$0.043-0.88$ mg/m^3
Volume of air collected	0.72 m^3
Standard curve range	$3.1-63.4$ µg/mL
Limit of detection (LOD)	0.018 µg/mL
Limit of quantification (LOQ)	0.053 µg/mL
Total precision of the test	5.56%
Total relative uncertainty	12.11%
Expanded uncertainty	24.22%

Also, the measurement of potassium bromate(V) concentration during the spectrophotometric determination of mercury in water was carried out at two stations in two different laboratories. A PN-EN ISO 17852 [7] standard-based fluorescence spectrometry method, used in the determination of mercury in water samples, requires the use of potassium bromate(V). The samples of potable water, surface water, underground water, or rainwater tested are subjected to chemical mineralization with released bromine and bromochloride (BrCl). Organic mercury compounds are brought to mercury(II). Immediately before performing the analysis, excess bromine is removed using hydroxylamine hydrochloride. From a sample mineralized in this manner, by performing a reduction with tin(II) chloride, mercury vapors are generated, which are blown out of the solution with a stream of inert gas (argon). Mercury, in the form of vapors, is determined by atomic fluorescence spectrometry.

During the collection of air samples, the laboratory technician was preparing a solution of potassium bromide, potassium bromate(V), to be used to mineralize and stabilize water samples. The $KBrO_3 + KBr$ solution was prepared by dissolving the analytical weighed amount (station 1) or by diluting the contents of the FIXANAL ampoule in water to one liter of volume (station 2). During the analysis, other chemical reagents were used at the stations: solution of tin chloride dihydrate ($SnCl_2 \cdot 2\ H_2O$), nitric acid (HNO_3), hydrochloric acid (HCl) for calibration, mercury chloride solutions ($HgCl_2$), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) (12%).

Sample 3 (station 3) was collected during the determination of bromates in water samples by ion chromatography in accordance with the PN-EN ISO 15061 standard [43]. The laboratory technician was preparing calibration solutions by diluting the potassium bromate(V) standard solution of a concentration of 1 µg/mL when the air sample was collected. During the analysis, other chemical reagents are also used: nitric acid (HNO_3), sulfuric acid(VI) (H_2SO_4).

The measurement of potassium bromate(V) concentration at station 4 was carried out during the determination of
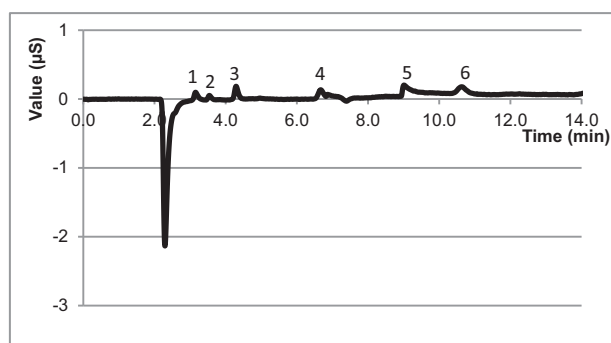

Fig. 3. Chromatogram of the solution obtained from analysis of air sample collected at station 3: (1) fluorides, (2) acetates, (3) chlorides, (4) nitrates (V), (5) phosphates(V), (6) sulfates(VI).

chlorprothixene in the medicinal product by means of potentiometric titration. During the preparation of the titrant, the employee has weighed 1.39103 g of pure potassium bromate(V) and then dissolved it in the water together with the weighted amount of potassium bromide. Direct titration of the prepared sample of the medicinal product using potassium bromate solution is carried out in a solution highly acidified with hydrochloric and acetic acid in the presence of potassium bromide until the titration endpoint is reached using potentiometric detection. The titration endpoint is determined potentiometrically using a combined platinum and calomel electrode ($Hg-Hg_2Cl_2$).

The following ions were found in the tested air samples:

- station 1 − fluoride, acetate, chloride, nitrite, nitrate(V), and sulfate ions,
- station 2 − fluoride, chloride, nitrate(V), and sulfate ions
- station 3 − fluoride, acetate, chloride, nitrate, phosphate, and sulfate ions (Fig. 3),
- station 4 − chloride, bromide, and nitrate ions.

No potassium bromate(V) presence was found as a result of the analysis of air samples collected in the air at the stations tested.

4. Conclusion

A method for determining potassium bromate(V) using ion chromatography with conductivity detection in the work environment air for the assessment of occupational exposure was developed. Tests were performed using Dionex IonPac® AS22 analytical column, with Dionex IonPac AG22 pre-column suitable for the determination of inorganic ions. The carrier phase providing the best isocratic separation conditions was a mixture of sodium bicarbonate and sodium carbonate. The proposed conditions of chromatographic separation allowed to carry out the determination of bromate ions in the presence of, among others, chlorides, bromides, acetates, nitrites, nitrates, phosphates, and sulfates.

For the determination of potassium bromate(V) present in the inhalable fraction of aerosol, a type IOM sampler with a filter made of mixed cellulose esters (MCE) was used. The developed method allows the determining of $KBrO_3$ in inhalable air fraction within the concentration range of $3.1-63.4$ µg/mL (i.e., $0.043-0.88$ mg/m^3 for a 0.72 m^3 air sample), that is at $0.1-2$ times the proposed MAC value.

The method shows a quantification of 0.00025 mg/m^3 when 0.72 m^3 of air is collected. The total uncertainty is 12%, while extended uncertainty is 24%.

The ion chromatography technique used to determine bromate ions is competitive in terms of sensitivity and selectivity compared to spectrophotometric methods. It enables selective determination of bromate ions in multi-ingredient mixtures of other inorganic ions at low concentration levels.

The developed method can be utilized to determine airborne potassium bromate(V) in the work environment with no influence on co-present inorganic ions.

Conflicts of interest

All authors have no conflicts of interest to declare.

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