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## COMPARISON OF TWO DIFFERENT ANALYTICAL PROCEDURES FOR DETERMINATION OF TOTAL MERCURY IN WET DEPOSITION SAMPLES

Comparison studies have been performed on determination of total mercury in wet deposition by two analytical methods. The studies were carried out in the period of March to November 2009 at the sampling point located near intensive traffic in Southern Poland (Zabrze). The difference between these two methods consisted in preparation of samples for analysis and in the type of measuring device. In both cases, the method of cold vapour atomic absorption spectrometry (CV-AAS) after reduction of SnCl<sub>2</sub> was used by means of a mercury analyzer model MA-2 produced by Nippon Instruments Corp. or of a mercury analyzer RA-915+ produced by LUMEX. Good agreement of the results have been obtained (relative error of the determination between the methods varied from 18% to 40%). Both analytical methods can be considered equivalent and used as a reference to each other. Quantity assessment of mercury wet deposition in southern Poland is lower than in 90 s, but still much higher in comparison with other countries in Europe and worldwide (ca. 30 µg·m<sup>-2</sup>·year<sup>-1</sup>).

### 1. INTRODUCTION

Elementary mercury, its inorganic salts and organic compounds belong to the group of metals responsible for trace but dangerous pollution of the environment [1]. Mercury is introduced to the environment from many anthropogenic and natural sources [2, 3]. Mercury emission in the ambient air in Poland in 2008 was about 15.7 Mg·year<sup>-1</sup> but in Silesia region it was ca. 2.7 Mg·year<sup>-1</sup> [4–6]. Mercury and its compounds emitted to the atmosphere may enter into chemical reactions both in gaseous and liquid phases with many pol-

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lutants present in ambient air [7–9]. Mercury is removed from the atmosphere in a form of wet and dry deposition [10, 11]. Wet deposition of mercury is primarily responsible for removal of this element from the atmosphere and re-depositing its compounds in water and soil and contributes to migration of Hg in the environment.

Content of mercury in the atmospheric precipitation or wet and dry deposition of mercury compounds is a topic poorly identified in the world. However, in countries such as Japan, Sweden and the United States, monitoring programs exist or existed to organize mercury deposition studies in designated research areas. In the period from 1995 to 1999, deposition of mercury was investigated in northern Sweden, Finland, Germany and Ireland. Annual wet deposition in those points ranged from 11.9 to 10  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  [12]. In Japan, the research of dry and wet deposition of mercury was carried out in the period from December 2002 to November 2003. Annual average wet deposition of mercury was  $12.8 \pm 3.9 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$ , and annual average dry deposition of mercury was  $8.0 \pm 2.7 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  [13]. In the United States the study of mercury wet deposition was conducted in Underhill in 1995–2006. During 11 years of investigation 1155 precipitation days were registered and the average monthly rainfall in this area ranged from 0.1 to 2.5  $\text{ng}\cdot\text{m}^{-2}$  [14]. Annual mercury wet deposition in the North-Eastern U.S. in 2002 ranged from 3.1 to 9.5  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  [15]. In the period from 1996 to 1997, the annual mercury wet deposition measured at air quality monitoring stations in IETU in Katowice (Poland) was 159  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$ , while the dry deposition was 48  $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  [16].

Two types of devices (classical funnels and automatic collectors) are used to collect samples for determination of trace amounts of analytes such as mercury, in samples of wet deposition [12–17]. Many analytical procedures are available for determination of mercury in various environmental samples, but for determination of mercury in precipitation usually one analytical technique is used [13, 16, 18–21]. The mercury concentration in precipitation and other liquid samples is measured by the cold-vapour atomic fluorescence spectrometry technique (CV-AFS), with  $\text{Hg}^0$  reduction by  $\text{SnCl}_2$  or  $\text{NaBH}_4$  as the reducing agent, or a method based on a AFS technique and concentration of mercury on gold traps and thermal desorption. The detection limit of this method for water samples or wet deposition was approximately from 0.02 to 0.1  $\text{pg}\cdot\text{cm}^{-3}$  [13, 22]. A different, described in literature analytical method to determine mercury in wet deposition is (CVAAS) [17]. The mercury concentration in the wet deposition is determined by a standard method based on reduction of all mercury by  $\text{SnCl}_2$  to elemental mercury after mineralisation of wet deposition samples.

## 2. EXPERIMENTAL

*Instrumentation.* In both cases a method of cold vapor atomic absorption spectrometry (CV-AAS) after reduction of  $\text{SnCl}_2$  was used. In the first of the methods

mercury analyzer Model MA-2 produced by Nippon Instruments Corp. was used, and in the second, mercury analyzer RA-915+ produced by LUMEX B.

*Method 1.* MA-2 analyser (Nippon Instruments Corp.) was used to determine gaseous mercury and particulate mercury. The determination was based on thermal decomposition of samples with gold-amalgamation of mercury vapours and detection by technique of non-dispersive double-beam cold-vapour atomic absorption spectrometry (CVAAS). The analyzer was equipped with RD-3 attachment to determine mercury after  $\text{SnCl}_2$  reduction. The light source was provided by low-pressure mercury discharge lamp with a thermostatic cell. Mercury vapour was transferred by internally produced carrier gas (ambient air purified by in-built carbon-filter) into quartz cell, where atomic absorption of mercury was measured at 253.7 nm. The total mercury content in the deposit was analysed by placing a ceramic boat with the filter into a sample heating furnace, where thermal sample decomposition took place at 700 °C. Decomposition products which might disrupt mercury determination were removed by appropriate additives (activated aluminium oxide and mixture of sodium carbonate and calcium hydroxide). Products of thermal decomposition were catalytically oxidized in a second furnace (850 °C). After passing through cleaning scrubbers and dehumidifier, the separated mercury vapours were directed to the heated gold trap. Then the trap was heated to 800 °C, and liberated mercury vapours were directed to quartz absorption cell where Hg content was measured.

*Method 2.* The RA-915+ (Lumex Ltd.) is a spectrometer for determination of mercury in various samples. Its operation is based on differential Zeeman atomic absorption spectrometry using high frequency modulation of light polarization. As a source of radiation ( $\lambda = 254$  nm) mercury lamp is used, placed in a permanent magnetic field. The mercury resonance line is split into three components (Zeeman mercury triplet:  $\pi$ ,  $\sigma_-$ ,  $\sigma_+$ ). When there is no mercury vapour in the analytical cell, the radiation intensities of both  $\sigma$  components are equal but when mercury atoms appear in the analytical cell, the difference between the intensities of the  $\sigma$  components increases with the increase of mercury vapour concentration. The method is used for determination of mercury in water and many other liquid samples. It is based on cold vapour technique. The attachment is equipped with 2 bubblers in which the sample is placed together with a known volume of the reducing agent. The reducing agent ( $\text{SnCl}_2$ ) changes  $\text{Hg}^{2+}$  to its atomic state. Mercury vapours are transported to the analytical cell where mercury atoms are directly detected.

*Sampling.* Wet deposition was collected in Southern Poland (Zabrze) at the point located near intensive traffic. Wet deposition was collected to a bulk sampler with an acid-washed open borosilicate glass bottle and a 82 mm funnel made of inert material. The funnel was supported in a thermostated housing system. In the summer, the samples are protected by the collecting system against solar radiation and impact of high

temperature, while in winter this system renders possible to maintain the samples in liquid state. The diagram of collector is presented in Fig. 1. Wet deposition was collected in various periods of time (6, 8, 14 days) at the level of 1.6 m above ground.

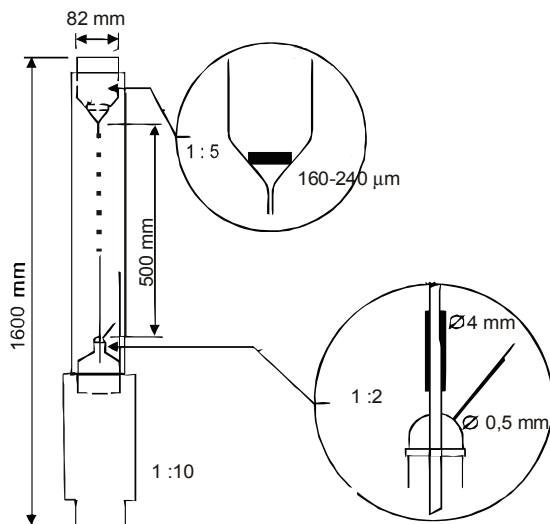


Fig. 1. Diagram of bulk samplers

*Reagents and materials.* Laboratory glass and all other equipment used in the analyses were digested with nitric acid (1:1) for 2 days and then washed in a laboratory washer (Miele G7883, Ontario). The solutions were prepared with highly deionized water whose conductivity was ca.  $0.5 \mu\text{S}\cdot\text{cm}^{-1}$ , Milli-Q (Millipore, Bedford, MA, USA). All reagents used in the analysis showed very low mercury content so that its impact on the final result can be neglected.

To prepare solutions for calibration, a certified reference material of the Hg ion concentration of  $1 \text{ g}\cdot\text{dm}^{-3}$  was used (Merck, Germany). For water sample storage, a stabilizing solution is required. This solution was produced by mixing  $50 \text{ cm}^3$  of concentrated nitric acid ( $\text{Hg} < 0.005 \text{ ppm}$ , pro analysis, Merck, Germany) and  $5 \text{ cm}^3$  of 4% solution of potassium dichromate ( $\text{Hg} \leq 0.000001\%$ , pro analysis, Merck, Germany), and then deionised water was added up to  $1000 \text{ cm}^3$ . The reduction solution, which presented mass concentration of  $50 \text{ g}\cdot\text{dm}^{-3}$ , was prepared by adding  $30 \text{ cm}^3$  of concentrated hydrochloric acid to  $50 \text{ cm}^3$  of deionised water ( $\text{Hg} < 0.001 \text{ ppm}$ , pro analysis, Merck, Germany). Then 5.0 g of tin chloride dehydrate was added ( $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ ) ( $\text{Hg} \leq 0.000001\%$ , pro analysis, Merck, Germany) and stirred carefully until the solution was completely dissolved. In the next step, deionised water was added up to the volume of  $100 \text{ cm}^3$ . Solution of potassium permanganate ( $\text{KMnO}_4$ ) of the mass concentration of  $25 \text{ g}\cdot\text{dm}^{-3}$  was prepared by adding 2.5 g of  $\text{KMnO}_4$  ( $\text{Hg} \leq 0.000005\%$ , pro analysis, Merck, Germany) to  $100 \text{ cm}^3$  of deionised water. So-

lution of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) of mass concentration of  $100 \text{ g}\cdot\text{dm}^{-3}$  was prepared by dissolving 5.0 g  $\text{NH}_2\text{OH}\cdot\text{HCl}$  ( $\text{Hg} \leq 0.000001\%$ , pro analysis, Merck, Germany) in deionised water and then filled up to the volume of  $50 \text{ cm}^3$ . Solution of potassium per(oxidi)sulphate ( $\text{K}_2\text{S}_2\text{O}_8$ ) of the mass concentration of  $40 \text{ g}\cdot\text{dm}^{-3}$  was prepared by dissolving 10.0 g of  $\text{K}_2\text{S}_2\text{O}_8$  (extra pure, Merck) in deionised water and filled up to the volume of  $250 \text{ cm}^3$ .

*Sample preparation for both methods.* For analyses by a MA-2 analyser wet deposition samples after collection were stabilized by addition of sulfuric acid 1:1 ( $2 \text{ cm}^3/100 \text{ cm}^3$ ).  $20 \text{ cm}^3$  of such solution were mineralized with  $\text{KMnO}_4$  solution in the Erleynmeyer flask in a water bath at  $90 \text{ }^\circ\text{C}$  for 2 h. After cooling, the excess of  $\text{KMnO}_4$  was reduced with  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , and the solution diluted to the volume of  $25 \text{ cm}^3$ . The measurements were twice repeated for each sample. Concentration of mercury was determined by the cold vapour atomic absorption spectrometry after reduction of  $\text{SnCl}_2$ . Entire volumes of samples were used in measurement. The standard curve ranged from 0 to  $2.5 \text{ ng Hg}$ .

For the analyses by a RA-915+ analyser  $1 \text{ cm}^3$  of the stabilizing solution ( $5 \text{ g}$  of  $\text{K}_2\text{Cr}_2\text{O}_7 + 500 \text{ cm}^3$  of  $\text{HNO}_3/1000 \text{ cm}^3$ ) was added to the samples.  $20 \text{ cm}^3$  samples were mineralized with  $0.2 \text{ cm}^3$  of potassium permanganate ( $25 \text{ g}\cdot\text{dm}^{-3}$ ),  $0.2 \text{ cm}^3$  of concentrated nitric acid and  $0.5 \text{ cm}^3$  ( $40 \text{ g}\cdot\text{dm}^{-3}$ ) of potassium per(oxidi)sulphate. Then the samples were heated in a water bath for 2 h at  $95 \text{ }^\circ\text{C}$ . After mineralization the samples were cooled down and then  $100 \text{ g}\cdot\text{dm}^{-3}$  of hydroxylamine hydrochloride was added dropwise to remove the excess of the oxidizer. The obtained solutions were placed in flasks of the volume of  $25 \text{ cm}^3$  and deionised water was added up to the scale mark. All samples were twice analysed. Concentration of mercury was determined by the cold vapour atomic absorption spectrometry after reduction of  $\text{SnCl}_2$ . To check the operation of the analyser, the calibration solutions were prepared from the reference material in the concentration range from 0 to  $300 \text{ ng}\cdot\text{dm}^{-3}$ . The linear correlation coefficient of the calibration curve  $R^2$  was 0.97504.

*Calculation of statistical parameters for both methods.* The detection limit (LOD) and quantification limit were determined by the analyses of ten independently prepared blank samples. Standard deviations of these samples were calculated and then the limit of detection and quantification of both methods were calculated under IUPAC recommendations according to the equation

$$\text{LOD} = t(\alpha, f) s \quad (1)$$

where  $t$  is the parameter of Student's  $t$ -test,  $f$  – number of degrees of freedom ( $f = n - 1$ ),  $n$  – number of independent samples, and  $\alpha$  – accepted level of significance. The limits of quantification values (LOQ) were calculated as multiples of detection limits ob-

tained for both methods. The repeatabilities of both methods were expressed as the level of precision under the same conditions of measurement and calculated according to equation:

$$r = t\sqrt{2}SD \quad (2)$$

where:  $t$  – parameter of Student's  $t$ -test, for  $\alpha = 0.05$   $t = 1.96$ . The recovery in both methods was determined by adding the appropriate amount of standard solution of mercury to the real samples, and subsequent analysis. The recoveries ( $R$ ) were calculated from the formula

$$R = \frac{C_T - C_0}{C_w} \times 100 \quad [\%] \quad (3)$$

where:  $C_T$  – concentration of mercury in the enriched sample,  $C_0$  – concentration of mercury in not enriched sample,  $C_w$  – amount of the added mercury. The expanded uncertainty  $U$  was calculated basing on the standard uncertainty ( $u_c$ ) and the coverage factor ( $k$ ) by the formula

$$U = ku_c \quad (4)$$

$k = 2$  was adopted (for normal distribution and probability  $p = 95\%$ ). Blank tests were carried out for both methods in a similar way as with the samples but instead of the sample proper volume of deionised water was added.

### 3. RESULTS AND DISCUSSION

#### 3.1. STATISTICAL COMPARISON OF TWO METHODS

Basic parameters obtained during validation of two analytical methods are presented in Table 1.

Table 1

Quality assurance of both analytical procedures

Parameter	MA-2 Nippon Instruments Corp.	RA-915+ Lumex
LOD, ng·cm <sup>-3</sup>	0.002	0.002
LOQ, ng·cm <sup>-3</sup>	0.005	0.005
Repeatability, %	5.9	9.4
Recovery, %	99.8	100.4
Expanded uncertainty, %	7	10

The results indicate that both methods represent similar limit of detection and quantification. Method 1 has a better repeatability of the results compared to method 2. The recovery rate in the first method was 99.8% and in the second was 100.4%. The recovery rates in both methods were at a similar level and slightly differed from the value taken as the actual one. Each method was also characterized by a different value of the analytical background of Hg. In the first method, the average concentration of mercury in blank samples was  $12 \text{ pg Hg}\cdot\text{cm}^{-3}$  and the concentration of mercury in blank samples produced by the second method was  $35 \text{ pg Hg}\cdot\text{cm}^{-3}$ . Nearly three-fold difference results from different ways of stabilization of samples. Concentrations of mercury were corrected for both methods with respect to values for blank samples. In the method 1, the solution of sulfuric acid 1+1 ( $2 \text{ cm}^3/100 \text{ cm}^3$  of solution) was added, in the method 2, nitric acid solution with potassium dichromate ( $5 \text{ g of K}_2\text{Cr}_2\text{O}_7 + 500 \text{ cm}^3$  of  $\text{HNO}_3/1000 \text{ cm}^3$  of deionised water) was added. In both methods different oxidized solutions during the digestion process of wet deposition were used (cf. sample preparation for both methods). Mineralization of samples in the method 2 is associated with several oxidants ( $\text{KMnO}_4$ ,  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{HNO}_3$ ). In the method 1, only  $\text{KMnO}_4$ , was used which led to lower contamination of the samples by reagents which contain trace amounts of mercury.

### 3.2. COMPARISON OF METHODS WITH ENVIRONMENTAL SAMPLES

The analysis of seven samples of wet deposition collected between March and November 2009 at the same point was performed. Data and exposition times of measurement series are presented in Table 2.

Table 2

Data of sampling

No.	Sampling time	Exposition time [day]	Amount of precipitation [cm <sup>3</sup> ]
1	13.03–21.03.2009	8	220
2	22.06–30.06.2009	8	430
3	16.06–30.06.2009	14	560
4	30.06–06.07.2009	6	210
5	14.07–28.07.2009	14	580
6	28.07–11.08.2009	14	550
7	20.10–03.11.2009	14	440

The volume of wet deposition samples collected ranged from  $210 \text{ cm}^3$  in a six-day collection cycle to  $580 \text{ cm}^3$  in a fourteen-day collection cycle. The concentrations of mercury in wet deposition samples and amount of wet deposition ( $\text{ng}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) are presented in Table 3.

Table 3

Mercury concentration in wet deposition  
and mercury daily wet deposition determined by two cold vapour techniques

No.	MA-2 [ng·cm <sup>-3</sup> ]	RA-915+ [ng·cm <sup>-3</sup> ]	MA-2 [ng·m <sup>-2</sup> ·d <sup>-1</sup> ]	[RA-915+ [ng·m <sup>-2</sup> ·d <sup>-1</sup> ]
1	0.024	0.017	103.8	73.5
2	0.220	0.181	1859.7	1530.0
3	no	no	no	no
4	<LOQ – (0.002)	0.019	no	104.6
5	no	no	no	no
6	0.005	<LOQ – (0.003)	30.9	no
7	0.006	no	29.7	no

In most of the cases, concentration of mercury in samples of wet deposition did not exceed the limit of detection of both analytical methods, which amounts to 0.02 ng·cm<sup>3</sup>. Total mercury concentrations in wet deposition analyzed by the method 1 (MA-2) ranged from <DL in samples 3 and 4 to 0.220 ng·cm<sup>-3</sup> for the sample 2 collected in the period from 22.06 to 30.06.2009. Total mercury concentrations in wet deposition analyzed by the method 2 (RA-915+) ranged from <DL in samples 3, 4 and 6 to 0.181 ng·cm<sup>-3</sup> in the sample 2 collected in the period from 22.06 to 30.06.2009. In most of the analyzed samples, the mercury concentrations of both analytical methods are similar to each other, and the resulting differences are at the acceptable level, e.g.: relative error (*R*) of determination, as observed between the methods, varied from 18% to 40%. It should be noted that for samples 6 and 7 the method 1 only provided possibilities for determination of mercury concentration, whereas for sample 4, only the second method was used. Mercury concentrations measured by the two analytical methods in wet deposition samples were converted into a daily value of wet deposition of mercury compounds. To calculate average values of mercury wet deposition, the samples below the limit of detection were considered as zero, the results are presented in Table 3 and Fig. 2.

The values of wet deposition of mercury compounds calculated based on the results by the first method are on average about 30% higher than those by the second method. The value of wet deposition of mercury compounds in sample 4 calculated from the method 1 is on average about 89% lower than the results produced by the second method.

The dispersion between the values of mercury wet deposition received by two analytical methods are presented in Fig. 3. The results are characterized by small dispersion in the measured concentration range. The resulting correlation coefficient between the values of wet depositions of mercury measured by the two methods is satisfactory and amounts to  $R^2 = 0.9971$  at the curve inclination  $s = 1.22$ . Relative error (*R*) of determination between the methods varied from 18% to 40%.



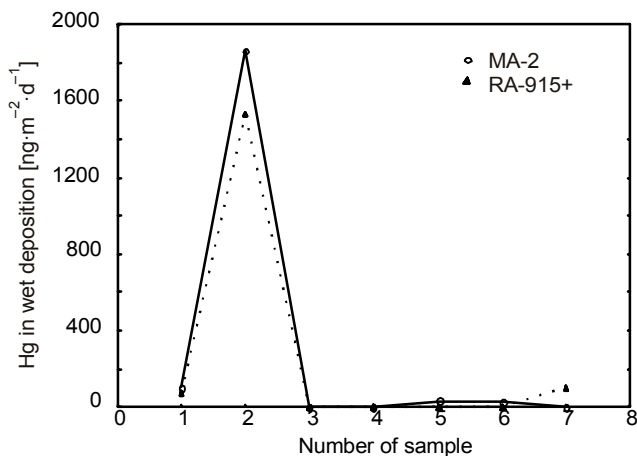


Fig. 2. Results produced by two analytical methods in seven samples

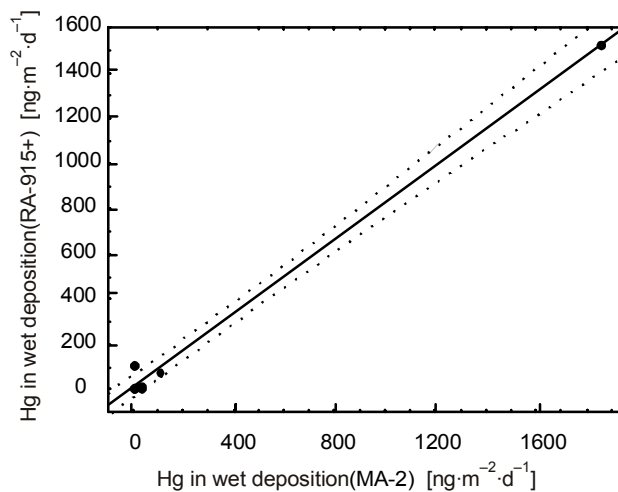


Fig. 3. Dispersion chart for results produced by two analytical methodology

The daily values of wet deposition of mercury compounds, as analyzed by the method 1 (MA-2), ranged from  $0 \text{ ng}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  (because the measured concentrations were  $< \text{DL}$ ) in samples 3 and 5 collected during 16.06–30.06 and 14.07–28.07.2009 to  $1859.7 \text{ ng}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  in sample 2 collected in the period from 22.06 to 30.06.2009. The daily values of wet deposition of mercury compounds analyzed by the method 2 (RA-915+) ranged from  $0 \text{ ng}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  in samples 3 and from 5 to 7 to  $1530.0 \text{ ng}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  in sample 2 collected in the period from 22.06 to 30.06.2009. The data on average concentration of mercury in wet deposition samples determined by both analytical methods and based on data about total annual amount of wet deposition (which in

Zabrze in 2009 was equal 7337 mm) were exploited to assess the total annual mercury wet deposition in the analyzed sampling point. The total annual value of mercury wet deposition measured by the first method was  $31.75 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$ , while the average daily value measured by the second method was  $26.94 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$ . Content of mercury in wet deposition in Southern Poland in 2009 is over five times lower than that in the same region in the past. During the period from 1996 to 1997, annual mercury wet deposition measured at the IETU air quality monitoring station in Katowice (Southern Poland) was  $159 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  [17]. However the annual mercury wet deposition in Zabrze is much higher than in other countries in Europe and worldwide. In measurement points located in European countries, Japan and United States mercury wet deposition ranged from 2.7 to  $12.8 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  [12, 13, 15]. The values obtained in the present work are comparable to those observed in China, where the estimated value wet deposition in 2006 ranged from 24.8 to  $39.6 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$  [22]. Increased level of mercury deposition is a result of the dominance of coal combustion in South Poland and in the primary structure of the Polish mercury emissions. Emission of mercury compounds into the atmosphere from coal combustion in thermal processes caused increase of mercury contribution associated with particulate matter, and consequently higher deposition of this element on the ground.

#### 4. CONCLUSIONS

- The applied analytical methods were characterized by good agreement of the results (relative error of determination between the methods varied from 18% to 40%),
- The values of wet deposition of mercury compounds calculated on the basis of results obtained by the first method (MA-2) in most cases were about 30% higher than the results by the second method (RA-915+),
- Method 1 is characterized by almost three-fold lower concentrations of Hg in the blank samples when compared to the method 2,
- The applied analytical methods of determination of mercury in wet deposition samples can be considered equivalent and used as a reference to each other.
- Quantity assessment of mercury wet deposition in southern Poland is lower than in 90 s, but still much higher in comparison with other countries in Europe and worldwide and was equal about  $30 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$ .

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