# Comparison of Results of Measuring Carbon Content of Atmospheric Aerosols by Methods of Reaction Gas Chromatography and Dry Burning

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## Abstract

Analysis has been conducted for 30 samples of atmospheric aerosols on glass-fibre filters with the use of reaction gas chromatography and dry burning method. It has been found that data for the content of total carbon that were obtained with two methods match among themselves within the limits of 30–50 %.

### INTRODUCTION

Carbonaceous particles include organic ($C_{org}$), elemental ($C_{el}$), and carbonate carbon. Organic and elemental carbon are important chemical ingredients of atmospheric aerosol (AA). "Elemental carbon" is considered to mean light-absorbing carbon that is spoken of as "black carbon" or "soot" in a number of publications. Particles of sooty carbon are fed into the atmosphere as a result of poor combustion of liquid and gas combustibles and due to forest fires. The works [1, 2] deal with catalytic activity of atmospheric elemental carbon. In addition, $C_{el}$ strongly absorbs sunshine and thus, it influences the radiation regime of the atmosphere. Both anthropogenic and natural sources may provide sources of organic carbon. Organic carbon can be also formed during atmospheric photochemical oxidation of gas hydrocarbons [3]. Many organic mixtures that are identified in aerosols contain compounds of different classes, including polyaromatic organic compounds, certain materials from this class being carcinogens [4].

The basis for methods to determine carbonaceous particles in an aerosol is a principle that has been described in [5]. Its essence consists in thermal separation of $C_{org}$ from $C_{el}$ and in the subsequent oxidation of every ingredient to form carbon dioxide that is converted to methane to be determined by a flame ionisation detector. The work [6] describes a method of thermal oxidation of carbonaceous particles by manganese dioxide $MnO_2$. The maximum temperature of oxidation of $C_{org}$ is as large as 525 °C, and 850 °C for $C_{el}$. $MnO_2$ is employed as an oxidiser that is in contact with the sample throughout the whole period of the analysis. The separation of $C_{org}$ and $C_{el}$ by a thermooptical analysis technique [7] occurs as follows. At first, a sample is subject to a progressive heat up from 120 to 550 °C in the atmosphere of He, and then it is burnt in an oxidising-inert atmosphere (2 % $O_2$ and 98 % He) in the range of 550 to 800 °C. The reflection factor is recorded with the use of a photodetector throughout the whole period of the analysis. The reflection factor declines during the course of the evaporation of organic

compounds in the inert atmosphere, which is due to the pyrolysis of the organic material. This fraction is classified as the organic carbon. Upon oxygen is added, the reflection factor rises, because the light-absorbing (elemental) carbon is burnt away and removed from the sample. The procedure of simple thermal separation [8] implies that as a sample is heated in an inert atmosphere, organic compounds are evaporated and are to be determined as $C_{org}$, and $C_{el}$, upon their combustion in the oxidising atmosphere.

The availability of various procedures to measure carbon in an aerosol and lack of definite calibrating standards leads to the necessity of performing the cross-laboratory measurements. The work [9] gives the results of the performed cross-laboratory analysis for $C_{org}$ and $C_{el}$ on quartz-fibre filters by a thermooptical method. Fundamental distinctions are discussed in the procedures to determine $C_{org}$ and $C_{el}$, because of which $C_{el}$ values that have been measured in the two laboratories differ from each other more than twice. The work [10] demonstrates that the values of total carbon content ($C_{tot}$) that have been received in 12 laboratories agree with each other within the limits of 20 %.

Comparison of the results that have been received by different methods is one of the problems of the research that is underway within the limits of the project "Aerosols of Siberia". The cross-laboratory analysis was conducted in the Institute of Chemical Kinetics and Combustion (IChKC), SB RAS, and in the Limnological Institute (LIN), SB RAS. The paper discusses the results that have been obtained during carbon measurements in AA by the two methods.

**MATERIALS AND METHODS**

AA samples were taken by means of a filter ventilation unit at a rate of 1.8 m³/h over the course of 1 day on GF 92 glass-fibre filters, 50 mm in diameter (manufactured in D-3354 Dassel, Germany). One half of the filter was used in determination of $C_{org}$ and $C_{el}$ by the method of reaction gas chromatography in IChKC, the other half, to determine the content of total carbon in the sample by the dry burning method in LIN. To make the comparison, 30

samples were used that have been taken in a settlement of Klyuchi (a suburb of Novosibirsk) from 20.04 to 20.05.2004, and two clean (background) filters.

The principle and the setup for the determination of organic and elemental carbon that were applied in this work are analogous to those described in [8]. To measure total carbon in AA, we employed a method that has been suggested by L. P. Krylova to determine organic carbon in solid residues of evaporated samples [11] and that has been modified later [12].

*Method of reaction gas chromatography*

The determination of organic and elemental carbon in AA was conducted in a setup (Fig. 1) that consists of a reactor *1*, an electroheating spiral *2*, a thermostat of the columns *3*, two gas valves *4*, *5*, a methanator, a detector of ionization in a flame (DIF), a gauge of small currents (IMT-05), and a recorder (KSP-4). In addition, the gas chromatograph "Tsvyet-100" is furnished with the temperature controllers (RT-09 and RT-17), with the blocks for the detector preparation (BPD-19) and gas preparation (BPX-1) that are necessary for the proper operation.

The reactor consists in a quartz tube, 50 cm long that is divided to three zones: that of the sample input, of the pyrolysis, and of the oxidation. The oxidation zone is filled with a catalyst, NiO on $Al_2O_3$. The tube (2/3 of its length) is warmed with an electroheating spiral, which has an effect that the temperature in the pyrolysis and oxidation zone is as large as 700 °C.

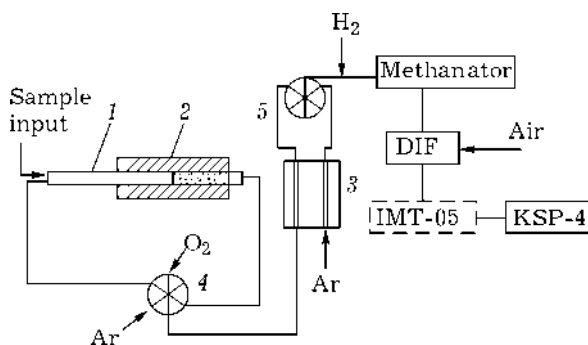The thermostat of columns contains two chromatographic columns, 3 m in length and



Fig. 1. Scheme of the set-up to determine organic and elemental carbon in atmospheric aerosols. For designations, see the text.

each of diameter 3 mm, filled with absorbent carbon. The temperature in the thermostat of columns comprises 125 °C.

The methanator is a steel tube, 30 cm in length and with the inner diameter of 4 mm that is filled with the catalyst, 12 % Ni on $Al_2O_3$. The methanator is placed in the thermostat of the detector, wherein the temperature is 300 °C.

A sample (1/4 part of the filter) is put in a quartz combustion boat with a steel tip. The quartz combustion boat with the sample is introduced into the reactor, which is flown through with a stream of the gas-carrier (argon) at a rate of 40 ml/min.

The quartz combustion boat is dragged to the pyrolysis zone with a magnet. During the course of 30 s at 700 °C, organic compounds are evaporated and transferred on the catalyst surface with the argon stream. Carbon dioxide, $CO_2$ that has been produced in the oxidation zone passes the chromatographic column through the gas valve 4. The gas to be analysed passes from the column through the gas valve 5 and mixes up with the stream of hydrogen (the rate of 30 ml/min) and then, it is fed into the methanator, where $CO_2$ converts to methane $CH_4$ at 300 °C. The stream of argon with the produced $CH_4$ is fed into the DIF. A signal of the detector is registered in a KSP-4 recorder by the gauge of small currents as a chromatographic peak. The determination of $C_{el}$ occurs in a similar way, but the gas valve 4 is previously closed, and the reactor is filled with oxygen, and then the valve is opened. Elemental carbon in the pyrolysis zone is oxidised with oxygen to form $CO_2$ and is fed from the reactor into the

column with the stream of argon. In methanator, $CO_2$ converts to methane that enters the detector. A solution of stearic acid of a known concentration was used as the reference substance to determine $C_{org}$, while a mixture of carbon black with aluminium oxide was used for $C_{el}$. The repeated analysis of standard tests has demonstrated that its accuracy comprises 5−10 %, and 20−25 % for AA samples. The detection limit is due to the background of a clean filter and it comprises 2−3 µg of carbon per sample when the signal-to-noise ratio is equal to 3 : 1. The duration of the analysis of a sample is 20 min.

*Method of dry burning*

A setup to determine total carbon (Fig. 2) includes the following parts: the electrocompressor *1*, absorption columns *2*, the device for air clearing *3*, two U-shaped tubes *4*, *5*, a combustion tube *6*, two electric furnaces *7*, *8*, an absorber for trapping nitrogen oxides *9*, an absorber to control for chlorides *10*, three Reberg vessels *11−13*. Absorption columns are filled with moisture absorbers (calcium chloride or magnesium perchlorate) and absorbers of air $CO_2$ (soda lime or Ascarite). The device for air clearing is intended for burning organic impurities in air oxygen. Its upper quartz part is filled with copper oxide (II) and it heats up to 700 °C; the bottom, heat-resistant or quartz part, is cooled by water that is poured in a beaker. U-shaped tubes are filled with Ascarite and calcium chloride. The horizontal quartz combustion tube, 450 mm in length is warmed with
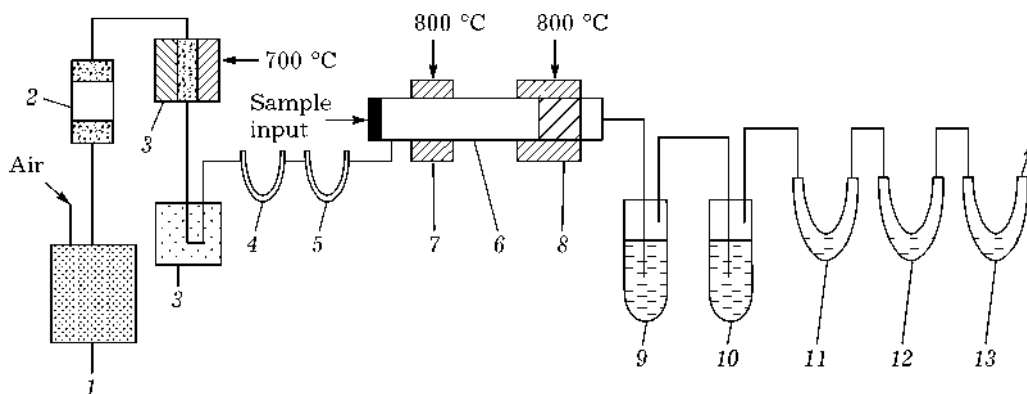


Fig. 2. Scheme of a set-up to determine total carbon in atmospheric aerosols. For designations, see the text.

two electric furnaces. The catalyst, in the form of two platinum plates $2 \times 5$ mm, is located in the second part of the tube and is warmed with a pipe-still heater to oxidize carbonaceous particles of a sample. The temperature in the burning tube is 800 °C. To trap nitrogen oxides, an absorber is attached that is filled with $K_2Cr_2O_7$ solution in concentrated $H_2SO_4$. The absorber to control for chlorides is filled with saturated $Ag_2SO_4$ solution in concentrated $H_2SO_4$. Three Reberg vessels that are filled with barium hydroxide $Ba(OH)_2$ solution are employed to absorb $CO_2$ that is produced upon the combustion of a sample.

Before the beginning of the work, the system is aerated over the course of 1 h with the furnaces turned on. Then solution of 0.01 M $Ba(OH)_2$ is brought in Reberg absorbers, 1.5 ml in each of them. The device for cleanliness checking is blown through with an incessant current of purified air over the course of 20 min. Thereafter, an excess of $Ba(OH)_2$ is titrated with 0.01 M HCl solution in the presence of phenolphthalein. Before the beginning of the analysis of a sample, the Reberg vessels are filled anew with $Ba(OH)_2$ solution in a current of purified air. A calcinated quartz cup with a filter (1/2 part) is put in the wide part of the horizontal quartz tube with a calcinated forceps in an incessant current of purified air. The tube aperture is tightly closed with a rubber stopper. First, the cup is warmed at the edge of the furnace; then the furnace 7 is brought close and the combustion proceeds at 800 °C over the course of 10 min. $CO_2$ blowing-off from the system goes on during $10-20$ min. An excess of $Ba(OH)_2$ in Reberg vessels is titrated with 0.01 M HCl solution with the phenolphthalein indicator. The same operation is performed with the pure filter so that carbon content is determined in the blank sample.

The quantitative content of total carbon of a sample is determined by the formula

$$C_{tot}\,(\mu g/\text{in the sample}) = [(A-B) + (A-C) + (A-D)] \cdot 60$$

where $A$ is the volume of 0.01 M HCl solution that has been consumed for the determination of the set-up cleanliness, ml; $B$, $C$, $D$ are the volumes of 0.01 M HCl solution that have been consumed for the determination of $Ba(OH)_2$ excess in Reberg absorbers, ml; 60 is the coefficient that corresponds to 1 ml of the

0.01 M HCl solution. This is a rather precise method: the relative standard deviation is 5 % with concentrations of $0.5-4$ mg C/l. The operation of the device is determined with standard solutions of glucose that is previously burnt with potassium persulphate.

## RESULTS AND DISCUSSION

The atmospheric aerosol is a complex diverse system in its chemical composition and size distribution; therefore, one of the problems during cross-laboratory measurements of, particularly, carbonaceous particles is lack of conventional calibrating standard. In this relation, it is impossible to estimate metrological characteristics of methods now in use if there are no reference samples. To compare the reproducibility of the two procedures, a variation factor ($V$) has been calculated that was equal to the ratio between the standard deviation ($s$) and the average $X$ magnitude (Table 1) for reference substances and for the AA samples. As it can be seen, the method of dry burning yields a greater instrumental error than does the method of reaction gas chromatography, which is more noticeable in the experiment with samples.

The Table 2 gives the results of the cross-laboratory analysis of 30 AA samples. It should be noted that the samples Nos. 17 and 28 with the maximum discrepancies have been excluded upon the comparison of the acquired data, together with the sample No. 27, since the filter itself was visually very black, and the 15 times difference is an evident error of the measurement. The correlation coefficient ($r$) between the $C_{tot}$ values in 27 samples comprises 0.83 (Fig. 3).

TABLE 1

Variation factor that was calculated for reference substances and for AA samples

| Method | $V$, % | |
|---|---|---|
| | Reference substances | AA samples |
| Dry burning (LIN) | 5 | 21.5 |
| Reaction gas chromatography (IChKC) | 3.4 | 10.5 |

TABLE 2

Results of measurements of the total carbon content of AA samples

| Filter number | $C_{tot}$, μg/filter | | $C_{tot}$ (LIN)/$C_{tot}$ (IChKC) |
|---|---|---|---|
| | LIN | IChKC | |
| 1 | 262 | 214 | 1.2 |
| 2 | 84 | 157 | 0.5 |
| 3 | 68 | 108 | 0.6 |
| 4 | 51 | 141 | 0.4 |
| 5 | 132 | 224 | 0.6 |
| 6 | 206 | 67 | 3.1 |
| 7 | 244 | 75 | 3.3 |
| 8 | 292 | 149 | 2 |
| 9 | 205 | 269 | 0.8 |
| 10 | 303 | 132 | 2.3 |
| 11 | 294 | 106 | 2.8 |
| 12 | 233 | 330 | 0.7 |
| 13 | 652 | 672 | 0.97 |
| 14 | 571 | 478 | 1.2 |
| 15 | 676 | 646 | 1.05 |
| 16 | 387 | 398 | 0.97 |
| 17 | 526 | 117 | 4.5 |
| 18 | 433 | 122 | 3.5 |
| 19 | 677 | 202 | 3.4 |
| 20 | 468 | 169 | 2.8 |
| 21 | 499 | 213 | 2.3 |
| 22 | 1183 | 478 | 2.5 |
| 23 | 2044 | 801 | 2.6 |
| 24 | 1183 | 615 | 1.9 |
| 25 | 2179 | 1373 | 1.6 |
| 26 | 791 | 820 | 0.96 |
| 27 | 70 | 1076 | 0.07 |
| 28 | 130 | 666 | 0.2 |
| 29 | 567 | 538 | 1.05 |
| 30 | 337 | 563 | 0.6 |
| Background 1 | 152 | 8 | |
| Background 2 | 148 | 10 | |
| Average background | 150 | 9 | |

It is evident from Table 2 that the ratio $C_{tot}$ (LIN)/$C_{tot}$ (IChKC) in the samples Nos. 13, 15, 16, 26, and 29 is close to unity. The data for the samples Nos. 1, 9, 12, and 14 agree well and the discrepancy in $C_{tot}$ values averages 22 %.
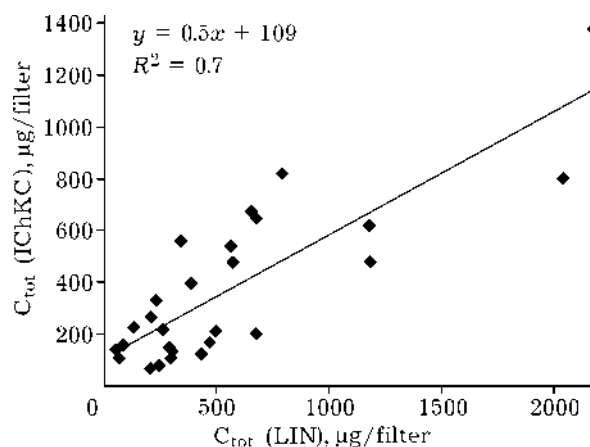


Fig. 3. Comparison of the results of measuring carbon content by two methods.

The differences between the measured data are fairly significant for certain samples and they comprise 40−50 %. Such scatter is evidenced both towards high carbon content that has been measured in LIN, as compared with IChKC, and *vice versa*. The discrepancy between the acquired data for the samples Nos. 8, 24, 25, and 30 may be caused by the inhomogeneity of the filter cake, as well as by the greater error of the method of dry burning, than the method that is applied in IChKC (see Table 1). To estimate how can vary the inhomogeneity of the filter cake, the filter at each laboratory has been divided into two parts, and the measurement has been conducted. It was recognized from the results of double analysis of certain AA samples that the reproducibility in the measurement by the method of reaction gas chromatography comprises 80−90 %, and that by the dry burning method does 60−80 %. The content $C_{tot}$ in the samples Nos. 2−5 that has been measured in LIN is approximately 2 times lower than the carbon content that has been measured by the method of reaction gas chromatography. It should be noted that the values that have been obtained in LIN for these samples are lower than the background value (*i.e.* than the value for the pure filter that has been measured by the method of dry burning).

The average value of the ratio $C_{tot}$ (LIN)/$C_{tot}$ (IChKC) for the remaining samples comprises 2.8. The correlation coefficient $r$ between two measurements is equal to 0.99. To estimate the legitimacy of the application of stearic acid solution as the calibrating standard in measure-
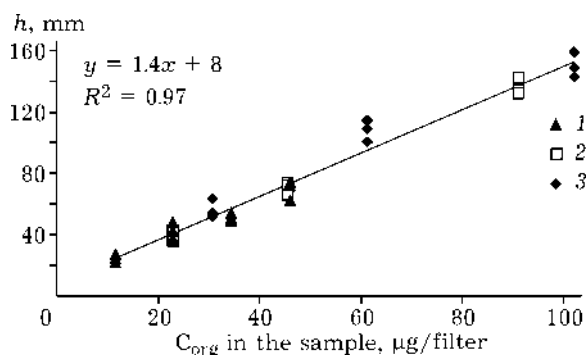
Fig. 4. Dependence of the height of chromatographic peak on $C_{org}$ content in the samples of a series of compounds with different concentrations: $1$ − benz(a)pyrene, $2$ − stearic acid, $3$ − oleinic acid.

ments by the method of reaction gas chromatography, oleinic acid and benz(a)pyrene have been studied additionally. As judged from literary data, these compounds have been determined in AA [4]. The data of Fig. 4 demonstrate that when calibrating based on each of these substances, the error does not exceed 10 %.

Let us note that the measurements for the AA samples and individual organic compounds by the method of reaction gas chromatography were performed with the catalyst NiO on $Al_2O_3$. To find out how complete is the oxidation of organic compounds and sooty carbon to $CO_2$, measurements have been conducted for the same individual organic compounds and for certain AA samples with the IC 12-73 catalyst. The catalyst constitutes a mixture of copper, nickel, and chrome oxides that is sprayed on $Al_2O_3$ particles. It has been registered that with this catalyst, the instrumental error did not exceed 5 % for individual compounds and 10 % for the samples.

During the analysis of a sample by the method of reaction gas chromatography with high $C_{el}$ content on the filter, a problem of its incomplete transformation into carbon dioxide appears, which leads to conservative figures that have been received for the carbon content on the filter. However, upon the repeated introduction of a quartz combustion boat with an already analysed filter into the pyrolysis zone of the reactor, the signal of the detector coincides with a signal from the pure quartz combustion boat. Thus, we can eliminate a factor of partial oxidation of $C_{el}$ that arises in certain cases and

leads to conservative results of the determination of the carbon content on the filter.

It will be remarked that the method of reaction gas chromatography is preferable for a quantitative estimation of carbon content in AA. One of the benefits of the method lies in the fact that individual determination of organic and elemental carbon is possible. This method is more precise and shows a good reproducibility as compared with the method of dry burning. In addition, the time for determination of a sample by two methods is equivalent (about 20 min), but when measuring $C_{tot}$ by the method of dry burning, a significant time is required to prepare the device for operation because of the necessity to make blow-down of the device over the course of 1 h before the work and change of the waste absorption vessels. In addition, to carry out the titrimetric procedure one needs to isolate carefully the reagents in use from their pollution. Thus, the method of dry burning is additionally a more time-consuming by comparison to the method of reaction gas chromatography.

**CONCLUSION**

The paper presents results of the analysis of 30 samples of atmospheric aerosols on fibreglass filters with the method of reaction gas chromatography and with the method of dry burning. Based on the results of the comparative analysis it has been pointed out that the data on the content of total carbon that have been obtained by the two methods correlate with each other within the limits of 30−50 %.

It has been demonstrated that the method of dry burning produces a greater error when compared to the method of reaction gas chromatography; therefore, the use of the latter method is more preferred for quantitative estimations.

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