



# Modification of hydrophobic sorbents by cobalt chloride in order to concentrate low molecular polar organic substances from the air for subsequent gas chromatographic determination



O.V. Rodinkov, G.A. Zhuravleva, A.S. Bugaichenko\*, M.I. Viktorova, V.N. Postnov, A.G. Novikov

Saint Petersburg State University, Institute of Chemistry, Russian Federation

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## ABSTRACT

The article presents a new method of modification of hydrophobic sorbents. To improve sorption pre-concentration of polar organic compounds in the air analysis, these sorbents are coated with cobalt chloride. This modification increases retention volume of lower alcohols by 5–10 fold as compared to that of unmodified sorbents and solves the problem of gas-chromatographic determination at 1–2 ppb (micrograms/m<sup>3</sup>) by using the most common flame ionization detector. It should be noted that the modification of hydrophobic sorbents by cobalt chloride has little influence on their porosimetry parameters (specific surface area, proportions of meso- and micropores) and modified sorbents are capable of retaining hydrophobic nonpolar and weakly polar analytes as well as original unmodified sorbents. Thus, a fairly simple procedure leads to a large positive effect.

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## 1. Introduction

Determination of organic compounds in the air at the limit level and at background concentrations usually includes a step of pre-concentration. Low molecular weight organic compounds, which are discussed in the article, are usually present in the air in their vaporized state. The main methods of concentrating vapors of volatile organic compounds (VOCs) are cryogenic concentration [1–3], solvent extraction, performed in the impinger [4] and denuders [5,6]; active [7,8] and passive [8,9] sorption of substances by sorbents contained in cartridges or tubes, as well as solid-phase microextraction (SPME) [10,11].

SPME and passive sampling are more suitable for prolonged atmospheric air control, rather than for operative monitoring the concentration of VOC, because of their inherent slow mass transfer. Solvent extraction suggests the use of liquid analysis methods and it is not suitable for determination of readily volatile substances such as methanol. A serious problem of cryogenic VOC pre-concentration is the interfering effect of moisture that condenses in the trap. Active sampling on solid sorbents (dynamic

sorption) is the most common and effective method of low molecular weight VOCs pre-concentration in the air analysis [7,8,12,13]. This is done by passing the analyzed air sample through a tube filled with sorbent. The absorbed VOCs are then desorbed by heating into a flow of carrier gas and transported to a gas chromatograph [13,14].

The greatest difficulties arise in the sorption pre-concentration of low molecular weight polar VOCs, such as methanol. All the known sorbents can poorly retain similar substances at room temperature. In this context previously suggested in gas chromatography sorbents based on salts of transition and alkaline earth metals appear to be the most promising [15]. In this context previously in gas chromatography suggested sorbents based on salts of transition and alkaline earth metals appear to be the most promising. However, these sorbents cannot provide retention of non-polar substances. According to the literature [16], these salts have a high solubility not only in water, but also in polar organic solvents. These solvents allow us to apply salts to non-water wet hydrophobic sorbents which are widely used for sorption pre-concentration of organic vapors in the air analysis [17].

The aim of this study was to evaluate the possibility of modifying the hydrophobic polymer sorbents by sorption-active, non-porous salts (SANS) and to assess their sorption properties with regard to retention of polar and non-polar volatile organic compounds.

\* Corresponding author. Tel.: +7 9217923442; fax: +7 8123080139.

E-mail address: [alexandrastepanjuk@gmail.com](mailto:alexandrastepanjuk@gmail.com) (A.S. Bugaichenko).

## 2. Experimental part

### 2.1. Reagents and preparation of solutions and model gas mixture

All the chemicals used in this work were of analytical reagent grade (Vekton Co. Ltd, St. Petersburg, Russia). Solutions of organic substances were prepared by a volume–volume methodology. Aliquots of analytes were collected using a measuring pipette, administered into a volumetric flask, wherein the level was brought to a flask label by addition of the required liquid (water, petrolatum oil). If necessary solutions thus prepared were diluted by pure liquid.

### 2.2. Sorbents

The study involved modification of various micro-, meso- and macroporous hydrophobic sorbents. We used microporous birch activated charcoal (BAC), synthesized from wood (30/50 mesh) [18]; spherical carbon molecular sieve Carboxen-1000 (45/60 mesh) (Supelco, Inc); mesoporous nonpolar polymeric sorbent Porapak QS (50/80 mesh) («Shrompack», EU); mesoporous polymer sorbent Polysorb-1 (0.25–0.5 mm) (Vekton Co. Ltd, St. Petersburg, Russia) – an analog of porapak Q; macroporous polymeric sorbent Tenax GR (35/60 mesh) (Supelco, Inc); agglomerate of multi-wall carbon nanotubes–baytubes C150P (0.1–1 mm) (Bayer Material Science AG, Germany), the carrier for the gas–liquid chromatography–Chromaton N-AW.

### 2.3. Modification of sorbents

In the process of hydrophobic sorbents modification, the calculated 0.25 g weighted quantity of cobalt chloride dehydrated by heating was dissolved in 5 ml of polar anhydrous ethanol and mixed with 0.5 g weighted quantity of sorbent by constant stirring. The selection of ethanol for applying cobalt chloride on hydrophobic sorbents is based on the fact that this salt is poorly soluble in non-polar solvents, and water cannot be used because it does not wet these sorbents. In Chromaton modification we used water solution of  $\text{CoCl}_2$ . The obtained mixture of the sorbent with a solution of cobalt chloride was evaporated over hot plate to loose state, then it was transferred into a drying oven and dried to constant weight at a temperature of 220 °C. The amount of coating salt was calculated via the weight increase of the sorbent, after it was sifted for separation of non coating salt. The proportion of non-separated salt equals 20–30% of the total amount of salt. The obtained sorbent was then filled in a tube with 3 mm inner diameter and a length of 7 cm.

### 2.4. Preparation of model gas mixture

The study of sorption properties of modified sorbents was carried out using the same model gas mixtures with known concentrations of test substances as for original sorbents. Model gas mixtures (MGM) having concentration with an order of magnitude of some  $\text{mg}/\text{m}^3$  were prepared in accord with the standard methodology by bubbling of carrier gas through liquid solutions having sufficiently big volume (over 1 L) and a given concentration of analytes  $C_0$ . Concentration of analytes in MGM  $C_G$  is given by equation:

$$C_G = C_0/K$$

where  $K$  stands for distribution coefficient in gas–liquid system [19]. Solutions based on water and ethylene-glycol were used for obtaining gas mixtures of polar substances (alcohols, ketones), and paraffinic oil was used for poorly water-soluble non-polar substances

(hexane, chloroform). Control concentration measurements of analytes in the generated MGM before and after experiments in all of the cases showed up only insignificant difference, thereby giving evidence of virtually constant concentration of analytes.

### 2.5. Evaluation of sorption properties of sorbents

This estimation was performed according to the standard method based on frontal technique [17]. A flow of the model gas mixture of tested VOC was directed to the sorption tube for concentration, and an effluent gas flow coming out of the sorption tube was directed into the dispensing loop (1  $\text{cm}^3$ ) of heated sampling valve. This valve was used for periodical withdrawal of the gas-phase samples and their injection into the gas chromatograph to determine the concentration of tested VOCs. On the obtained chromatograms we measured the heights of the peaks of analytes ( $h$ ) and then compared them to the heights of the peaks obtained at injecting into the chromatograph the model gas mixture, directed to the sorption tube ( $h_0$ ). Within the linear dependence of the detector signal on the analyte concentration, the value  $h/h_0$  is equal to the value  $c/c_0$ , where  $c$  and  $c_0$  are analyte concentrations at the outlet of the sorption tube and the inlet, respectively. We plotted output curves of tested VOCs retention as dependences of  $c/c_0$  on  $V$ , where  $V$  is the volume of gas passed through the tube. From these curves we determined the retention volume ( $V_R$ ) and the breakthrough volume ( $V_B$ ). The retention volume and the breakthrough volume were taken equal to the volumes of model gas mixture transmitted through the sorption tube, for which the following conditions are satisfied:  $c/c_0=0.5$  and  $c/c_0=0.05$ , correspondingly.

### 2.6. Instruments

Determination of VOCs was carried out using a gas chromatograph "Kristall 5000.2" (product of "Chromatec", Russia) equipped with a flame ionization detector and a capillary column DB-1 (60 m  $\times$  0.53 mm ID  $\times$  3  $\mu\text{m}$   $d_f$ ). The surface area and porous structure of the original and modified cobalt chloride sorbents were investigated using Accelerated Surface Area and Porosimetry System ASAP 2020MP (Micromeritics Instrument Corp.). This system allows us to analyze the size distribution of not only mesopores, but also of micropores in the range of 0.35–2 nm. Nitrogen was used as the carrier gas.

## 3. Results and discussion

### 3.1. The laws of VOCs retention from the gas phase by sorbents modified with cobalt chloride

Previously [20], we have found that many completely dehydrated salts of transition and alkaline earth metals have the property of strong retention of polar VOC vapors. The most probable mechanism of this retention is the ion–dipole interaction between the VOCs molecules and nodes of the salts crystal lattice. A detailed study showed that  $\text{Mg}(\text{ClO}_4)_2$  provides the strongest retention of methanol vapor and acetone. However, this salt completely loses water of crystallization at temperatures above 250 °C, which is not compatible with the use of many hydrophobic and, in particular, polymeric sorbents. For this reason, we have chosen  $\text{CoCl}_2$  as SANS, which although ranking 30–50% below magnesium perchlorate in sorption capacity, completely loses water of crystallization even at 150 °C.

As a result of our research it was found that the modification of hydrophobic sorbents by cobalt chloride leads to a multiple increase in methanol retention volumes (Table 1). Upon that the

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