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Abstract

The anhydrous potassium fluoride was proposed as a novel selective moisture trapping agent for gas chromatography to remove water vapor during adsorption concentration of low molecular weight volatile organic compounds (VOC) from the moist air. Unlike the traditional desiccants potassium fluoride does not adsorb alcohols and ketones. To improve the adsorption efficiency the analyzed air stream was purged through two sequential traps. The first trap was filled with a desiccant based on potassium fluoride and the second trap contained a sorbent to retain low molecular weight VOCs such as methanol and acetone. The adsorption of VOCs was followed by a thermal desorption from the second trap into the gas chromatographic column for analysis with a flame ionization detector. The proposed moisture trapping and preconcentration assembly allows determining the low molecular weight VOCs at the levels of μ g/m3 with RSD not exceeding 5 % after 4-8 minutes of preconcentration.

Key Words

Sorption concentration, desiccant, thermal desorption, gas chromatographic analysis, moist air, polar organic compounds, potassium fluoride

INTRODUCTION

The gas chromatographic analysis of background levels of volatile organic compounds (VOCs) in the air usually requires steps of preconcentration. The methods employed for VOC preconcentration from the air include the following: cryogenic sample pre-concentration [1]; solvent extraction, implemented in impingers [2] and denuders [3]; active [4,5] and passive [5,6] sample enrichment on solid adsorption badges and packed tubes; solid phase micro-extraction (SPME) [7,8] and a recently developed method of chromatomembrane preconcentration of polar VOC [9]. A substantial shortcoming of cryogenic sample pre-concentration involves the formation of ice crystallites during analysis of the humid air. The SPME and passive sampling in view of the inherent slow mass transfer are more relevant for long-term monitoring of the air, rather than for real-time control of the pollutants. Solvent extraction is oriented towards usage of liquid analysis methodologies and does not fit to determining volatile compounds such as methanol. Active sample enrichment on solid sorbents (solid-phase extraction [4,5,10]. VOC with the boiling point below 200 °C can be recovered from a sorbent by thermal desorption [5,11] followed by gas chromatography.

Compositional surface-layered sorbents [12] open new opportunities by improving efficiency of SPE during air analysis.

The water vapor has an adverse impact on VOC concentration from the air [13]. The higher the water vapor concentration in the air the lower the retention of the majority of VOCs at the time of preconcentration. During thermal desorption, water vapor increases the peak-width of the analytes. This problem has been discussed extensively in reviews [15,16]. To circumvent the negative water interferences many different approaches have been developed. These include passing the sample through a moisture trap filled with a dehydrating agent, removal of the water prior to the sampling or after analytes thermal desorption.

To remove water vapor from the analyzed air containing VOC, four major methods are introduced in the literature [17,18]: adsorption using hydrophilic adsorbents (silica gels, molecular sieves and aluminum oxide); sorption with hygroscopic salts (Mg(ClO₄)₂, Ascarite, K₂CO₃, CaSO₄, Ba(ClO₄)₂, Na₂SO₄); cryogenic trapping and water removal using membrane tubes made of perfluorinated ion-exchange resin. The common limitation for the known water removal methods is the retention of polar organic substances such as low molecular alcohols during the water retention process.

Various authors [19,20] critically reviewed various drying methods and advocated the dry purging. This technique involves purging of the dry gas through sampling tubes after sampling has taken place in order to remove water vapor while retaining analytes prior to thermal desorption. As far as we know, such a method was used more than thirty years ago to remove water adsorbed on Tenax [21]. Tenax adsorber does not contain any desiccants. The two-step preconcentrator was suggested for the analysis of the exhaled gas of human breath [22] to perform VOCs concentration and water vapor removal from samples. Despite the considerable ingenuity, there are significant limitations present in the described dehydrating methods due to the loss of VOCs or introduction of contaminants into the analyzed systems. Particularly this problem is manifested in the determination of lower molecular weight plar VOCs such as lower molecular weight alcohols and ketones. Higher specific surface area is required for sorption concentration of lower molecular weight alcohols and ketones and ketones. Hydrophilic sorbent such as carbon in particular active charcoal has a higher specific surface area and known in the art to be the preferred sorbent for lower molecular weight polar VOCs [23].

The advantages and disadvantages of various moisture removing techniques during the VOC concentration are described in [14]. During the process of moisture removal various issues may occur due to the hydrolysis at the surface of the polar sorbents resulting in blocking the cryo-trap in cryo focusing and interfering with the chromatographic process (e.g. damage of the stationary phase). The moisture removing traps packed with mentioned above hydrophilic salts can be used in front of the adsorbent trap or cryo-trap. The advantages of these drying traps include a high degree of the drying and also high flow rate while purging the analyzed air through the traps. The nafion membrane is another example of a dryer with even higher capacity with respect to water vapor; nafion membranes are established to remove moisture from air samples. Nafion is an ionic copolymer of tetrafluoroethylene (Teflon) and a fluorosulfonic acid group. Each sulfonic acid group can co-ordinate up to 13 molecules of water causing the selective permeability for water [24]. However both types of moisture traps based on hydrophilic salts and the nafion membranes absorb molecules of alcohol, acetone and ethyl acetate [25].

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This work aims to search a hygroscopic salt which does not retain polar organic compounds and increases the sorption preconcentration efficacy during the gas chromatographic analysis of the moist air. Conventional drying materials are not effective in this case because they tend to retain polar organic compounds, in particular lower aliphatic alcohols and ketones [18, 26].

EXPERIMENTAL AND PROCEDURE

Chemicals and preparation of solutions

Methanol, ethanol, acetone, methylethyl ketone and inorganic salts (KF, NaCl, K₂CO₃, CuSO₄, CaCl₂, CoCl₂, Mg(ClO₄)₂) were purchased from Ltd. Vekton (Saint-Petersburg, Russian Federation). All purchased solvents were of high purity and were handled according to the safety guidelines. DI water was used for all aqueous solutions. All of the aqueous solutions were prepared by a volume–volume and mass–volume methods. Aliquot of analytes or salt weight were collected using a measuring pipette or analytical balance, administered in to a volumetric flask where the dilution with distilled water was performed.

Preparation of model gas mixtures

To conduct the experiment it was decided to choose the most rational method of obtaining model (standard) gas mixtures (MGMs). Static and dynamic procedures can be used for the preparation of MGMs [27]. Indeed static procedures imitate the preparation procedure for standard solutions based on the dilution of the known amount of target components with the diluent gas. Moreover, adsorption on the walls of the vessel in which MGMs are prepared has a negative effect in static procedures. Because of this, MGMs with trace concentrations of the target components are difficult to prepare. Dynamic procedures are based on the continuous introduction of target components into the diluent gas flow. They can be subdivided into nonequilibrium and equilibrium procedures. In the nonequilibrium procedures, the target components diffuse at a constant rate from a liquid or gas phase into the diluent gas flow through a membrane [28] or capillary [29]. The long time taken to reach steady-state conditions in the generation of MGMs and difficulties in the production of mixtures with specified concentrations are the disadvantages of these procedures. The equilibrium procedures are based on the saturation of the diluent gas flow with target components in contact with a generation solution of given concentrations of the components [30]. The main advantage of equilibrium procedures is concentration indifference of MGMs target components to the diluent gas flow rate. The volume of a generated MGMS can be increased several times by multistage extraction, in which the diluent gas passes through a few bubblers filled with a generation solution placed in series [31]. opportunities were discovered when MGMs were Additional generated using chromatomembrane cells modified with active carbon [32].

In this work MGMs were generated having concentrations with an order of magnitude of a few mg/m3 and were prepared in accord with the standard methodology by bubbling a carriergas through aqueous or ethylene glycol aqueous solutions of the sufficiently large volume (over 1L) with a given concentration of analytes C_0 . The concentration of analytes in a MGM (C_G) was calculated as follows:

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 $C_{G} = C_{0}K$

(1)

where K is a distribution coefficient in a gas–liquid system [30]. Control samples concentrations of analytes in the prepared MGMs before and after experiments were defined and measured showing insignificant difference thereby providing evidence of virtually constant concentration of analytes. Relative humidity (RH) of the MGM was regulated by adding ethylene glycol to aqueous solutions of the tested polar compounds. Molar concentrations of ethylene glycol in aqueous solution were 0.75M and 0.5M to obtain 25%RH and 50% RH respectively. Analytes concentration in model gas mixtures was $(50 \pm 5) \text{ mg/m}^3$.

Preparation of Sorbents

To increase the specific surface area the tested sorbent was applied from the aqueous salt solution onto the gas chromatographic diatomite carrier Chromaton N (NAW) with the particles size of 0.5 - 1.0 mm in the amount of 30 mass %. The carrier mass of 1 g was combined with 5 ml of aqueous salt solution followed by continues mixing and water evaporation over the hot plate. The prepared sorbent was placed in the oven at 250° C to obtain the constant mass and was stored later in a hermetically sealed bottle. To test the moisture trapping properties, stainless-steel tube 5cm x 0.3 cm was filled with the tested sorbent and the wet air flow of model gas mixtures was purged through the filled moisture trap at the rate of 200 ml/min to the second trap with activated carbon where organic compounds such as methanol and acetone were adsorbed.

Sorbent Capacity Analysis

Water trapping capacity was determined by gravimetric analysis. The analyzed air flow was moistened by purging air through a 1% aqueous solution of NaCl prior entering the trap filled with a tested drying agent. Sodium chloride was added to DI water in order to prevent condensation in the trap. Purging air through 1% NaCl aqueous solution provided 99 % RH to the MGM. Temperature was 20°C while conducting experiments. To test the water trapping capacity moisturized air flow was purged to two traps. The first one was filled with the tested moisture trapping agent, and the second trap was filled with calcium chloride to fully adsorb water vapors that didn't retain in the first trap. Upon purging a definite air volume, the second trap with $CaCl_2$ was weighed, and the breakthrough volume (V_B) of water vapor through the tested trapping agent in the first tube was found.

Sorption Concentration and Chromatographic Technique

Analyzed gas flow or MGM was purged from the drying trap to the sorption trap and to the injection loop (1 mL) of the heated sampling valve of a gas chromatograph. Sampling valve was used to periodically inject the analyzed air sample to the chromatograph. In this work "Tsvet 500 M" gas chromatograph with FID was used. The stainless steel column packed with 80/100 Chromosorb-101 was 100 cm in length and with the internal diameter of 0.3 cm. The analyte peak heights (h) were measured and referred to the peak heights of the model gas mixture (h₀). Within the linearity range of a detector signal, the h/h₀ value equals to c/c₀ value, where c and c₀ are analyte concentrations at the exit and entrance of sorption tube respectively. Output graphs of the adsorbed test compounds were plotted as a function of c/c₀ to the V, where V is the gas volume purged through the tube. Breakthrough volume V_B was found experimentally from the

plotted graphs and it was determined as a carrier gas volume that corresponds with 95% extraction of the analyte from the tested sample.

RESULTS AND DISCUSSION

Effect of the Air Relative Humidity on Retention of Polar Organic Compounds on Activated Carbons

Activated carbon is the most effective known adsorbent for the concentration of low molecular weight polar organic compounds such as lower weight alcohols and ketones. Gaseous and easily volatile compounds with the boiling temperature below (50–80) °C can be recovered from these sorbents by thermal desorption [5,26]. The highest hydrophobicity along with the minimum catalvtic activity is applicable for birch а activated charcoal (BAC) synthesized from the wood [33]. Unlike polar polymer adsorbents, activated carbons have relatively low adsorption affinity towards aqueous vapor and can be applied to extraction of organic substances from humid air. Nonetheless, while applying thermal desorption it would make sense to perform preliminary drying of the analyzed air by letting it pass through the pre-tube filled with a desiccant [34]. Retention of polar organic compounds on activated coconut charcoal carbons significantly depends on the analyzed air humidity. Figure 1 shows retention curves of methanol at different relative humidity.

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Figure 1. Methanol retention curves at the following humidity at 20°C: 1 - 99 % RH; 2 - 50 % RH; 3 - 25 % RH.

Thus, the pre-drying must significantly increase the effectiveness of organic substances sorption concentration and increase the breakthrough volumes.

Comparative Analysis of Inorganic Salts Solubility and Respective Breakthrough Volumes of Vapors of Water and Methanol

The various hygroscopic inorganic salts form crystalline hydrates with several water molecules can be considered as potential air dehydrators. However many of them tend to retain polar organic compounds making hydrates unsuitable for polar organic compounds determination by gas chromatography. When searching for the salt to selectively retain water vapor, it is reasonable to use salt's property to form crystalline hydrates and its solubility in water. It has been previously established that only salts easily soluble in alcohols extract alcohols from gaseous phase. Investigating the solubility of various salts in water and methanol, we found [26] that only salt poorly soluble in alcohols but soluble in water may form crystalline hydrates at ambient temperature and can be regarded as a drying agent to retain water vapor selectively and not adsorbing any alcohols. Potassium fluoride proved to selectively retain water therefore suggesting a new application as a moist trapping agent for detecting low molecular polar organic compounds by gas chromatography.

The solubility values of the tested salts in water and methanol are presented in Table 1. Salts were chosen based on its hygroscopic properties to form crystalline hydrates. Breakthrough volumes (V_B) of water vapor and methanol were found as described here above and presented in the Table 1. Potassium fluoride has the low molecular weight and forms crystalline hydrates with 4 water molecules at the ambient temperature. It was found that potassium fluoride is an optimal selective moisture trapping agent that has no selectivity to methanol. Breakthrough volume of water vapor through KF-filled trap is similar to the one filled with CaCl₂. However CaCl₂ showed the capacity to retain low molecular weight alcohol as oppose to higher selectivity of KF to retain water only. As it is clear from the Table 1 sorption capacity of KF to water vapor is by several times greater than the sorption capacity of potassium carbonate (K₂CO₃) recently suggested for selective water sorption [35].

Table 1. The comparative analysis of inorganic salts solubility and respective breakthrough volumes of water and methanol at 20°C through the tested salts.

Salt	The salt solubility, at 293 K, g L ⁻¹ [36]		The breakthrough volume, L g ⁻¹		
	in water	in methanol	water	methanol	
			$V_{\scriptscriptstyle B}$	VB	
KF	949	1.9	27.2 ± 1.3	< 0.05	
K_2CO_3	1110	< 0.1	7.1 ± 0.4	< 0.05	
CuSO ₄	320	10.4	1.0 ± 0.06	0.08 ± 0.005	

$CaCl_2$ 7	45	299	30.1 ± 1.4	2.5 ± 0.1
CoCl ₂ 5	29	385	12.0± 0.5	3.6 ± 0.2
Mg(ClO ₄) ₂ 9	92	518	12.2 ± 0.7	6.5 ± 0.4

Table 1 suggests that KF is the most effective selective moisture trapping agent to adsorb polar compounds from the air for use in gas chromatography. When compared to K_2CO_3 , $CuSO_4$, $CaCl_2$, $CoCl_2$, $Mg(ClO_4)_2$, potassium fluoride KF capacity to retain water is similar to conventional $CaCl_2$ with advantage of not retaining other polar compounds allowing to detect polar compounds in the air with higher precision eliminating the interference with water.

Sorption Concentration of Organic Compounds from the Moist Air followed by a thermal desorption and gas chromatographic analysis

As described above, potassium fluoride ability to retain water vapor selectively makes it a viable KF-based sorbent to trap moisture during sorption concentration of polar organic compounds with a purpose of GC analysis thereof. In such a case, analyzed air is to be purged through two sorbing traps, the first one is filled with KF-based adsorbent, and the other one is filled with the activated charcoal to adsorb the analytes from the air during preconcentration (Figure 2, a).



Figure 2. The schematic diagram of polar organic compounds sorption concentration from the moist air (a) followed by a thermal desorption and GC analysis (b): 1 - analyzed air inlet; 2 - drying trap with KF-based sorbent; 3 - adsorption trap with activated charcoal; 4 - electrical pump; 5 - analyzed air outlet; 6 - carrier gas inlet; 7 - sampling valve of the gas chromatographer; 8 - electric heater; 9 - chromatographic column; 10 - detector (FID).

After the purging of the defined air volume at the defined air flow rate the adsorption trap (3) (Figure 2. b) was placed into position of a batching loop of the heated batcher-valve (7). The adsorption trap was heated (duration 90 s) by a slot-like oven (8). Thereafter the batching valve was set into a position designated by dashed lines in Figure 2 b for 30 seconds. Over this time analytes desorbed by the heating were purged from the adsorption trap into the gas-chromatographic column (9) and further into the detector (10). After that the batching valve was set into an initial position. The performed studies showed that quantitative (above 95%) thermal

desorption from the surface of activated charcoal into gas-carrier takes place in the temperature range (280–300) °C for thermo-stable organic substances having boiling temperatures below 80 °C.

Figure 3 illustrates retention curves for the methanol and acetone (2, 4) from the moisture air (99 % RH) using KF-based drying trap. These curves were compared to the ones obtained without drying (1, 3) for methanol and acetone. As a result, the suggested approach of sorption concentration with preliminary air dehydration is proved to increase the retaining characteristics for polar organic compounds by several times. In this work, breakthrough volumes increased 7 times for methanol and 2.5 times for acetone when KF was used in the moisture trap.

C/C

1,0

0,8

0,6

0,4

0,2

0,0



V, l

. . The preliminary moisture removal using KF trap eliminates the negative effect of water vapor, not only at the stage of sorption concentration, but also at later stages of thermal desorption and GC analysis. Fig. 4 compares two chromatograms obtained by thermal desorption at 280 ^oC of 20 mg/m3 analytes alcohols sorbed from 3 liter of moist air at 99% RH with preliminary water removal (a) and without using the KF moisture trap (b). All other conditions were kept the same.

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Fig. 4. The chromatograms obtained after the thermal desorption of alcohols adsorbed from moist air using KF moisture trap (a) and without moisture trap (b) where 1 - Water; 2 - Methanol; 3 - Ethanol. The column with Chromosorb-101 (80-100 mesh) 100x0.3 cm, temperature of 140 °C, FID was used.

Validation Procedure, Quality Assurance and Quality Control (QA/QC)

The analytes concentration in the analyzed air was calculated using the following formula:

$$C_{G} = SF/V \tag{2}$$

Where S is the area of the analyte peak in the chromatogram; F is the coefficient of proportionality of the peak area and the amount of analyte injected into the chromatograph (calculated at the calibration); V - volume of analyzed air purged through the sorption trap.

To verify the devised methodology a series of experimental determination of analytes was performed regarding MGMs with known concentrations (Table 2). As it is seen in Table 2 discrepancies between experimentally determined (Eq. (2) and known (by virtue of Eq. (1)) analytes concentrations are insignificant with respect to the background of random scatter of the analysis results, the relative standard deviation (RSD) is less than 5 %.

Table 2. The mean values of volatile organic compounds recovery from MGM (n = 4, confidence probability = 0.95) and RSDs, relative standard deviations (repeatability).

Compound	Calculated in accord	Experimentally determined Eq.	RSD	Recovery
	with Eq.(1) $\mu g/m^3$	(2) μ g/m ³ +/- random error	(%)	(%)
Methanol	128	123 ± 7	3.7	96
	6.4	6.0 ± 0.4	4.6	94
Ethanol	142	138 ± 7	3.4	97

	7.1	7.4 ± 0.5	4.3	104
Acetone	132	128 ± 6	3.0	97
	6.6	6.2 ± 0.4	3.8	94
Methylethyl	166	158 ± 10	3.9	95
ketone				
	8.3	7.7 ± 0.6	4.6	93

Considering a multistep process of analyte recovery, the relative combined uncertainty u_r of the measurement result can be evaluated using the following formula [37]:

$$u_r = \sqrt{(u_{r(V)})^2 + (u_{r(cal)})^2 + (u_{r(rec)})^2 + (u_{r(rep)})^2 + (u_{r(LOD)})^2}$$
(3)

where: $u_{r(V)}$ – relative standard uncertainty of a sample volume (the same for all analytes), $u_{r(cal)}$ – relative standard uncertainty of calibration step, $u_{r(rec)}$ – relative standard uncertainty of recovery determination, $u_{r(rep)}$ – relative standard uncertainty of repeatability, $u_{r(LOD)}$ – relative standard uncertainty of limit of detection (LOD).

$$u_{r(rep)} = \frac{RSD}{\sqrt{n}}$$
$$u_{r(LD)} = \frac{LOD}{C_G}$$

The high recovery values from the table 2 allow to neglect relative standard uncertainty of recovery determination $u_{r(rec)}$ while the high linearity of the used flame-ionization detector allow to omit the value of $u_{r(cal)}$ in the equation (3). The relative standard uncertainty of a sample volume $u_{r(V)}$ should be considered. The value of $u_{r(V)}$ is based on the uncertainty of the measurement of flow rate through the tube (5 %).

The characteristics of methodologies for gas chromatographic determination of organic substances vapors using sorption pre-concentration on the devised procedure are given in Table 3. LOD for every analyte was calculated using the following 3σ formula:

$$LOD = \frac{LOD_m}{V_G} = \frac{3\sigma m_{st}}{h_{st}V_G}$$

where LOD_m – limit of detection of a particular analyte mass when injecting it to the chromatograph, μg ; V_G – the sample volume of the analyzed air purged through the sorption tube, m³; σ - the noise of the detector (mV), h_{st} – the signal amplitude of analyte pick (mV) for the standard solution, where analyte mass is m_{st} , μg .

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Table 3. The characteristics of methodologies for determining VOC in the air by use of sorption preconcentration and flame-ionization detection. The sorbent is the activated coconut charcoal, the tube is 5 cm x 0.3 cm; t – preconcentration duration; V_{sam} = sample volume; LOD = limit of detection; RSD – relative standard deviation at C_G = 5LOD

Compound	V _{sam} , L	t, min	LOD	RSD,	u _{r(V)} ,
			µg/m³	%	%
Methanol	1	4	4	6.5	5.0
Ethanol	2	6	2	5.8	
Acetone	4	8	1	5.3	
Methylethyl ketone	4	8	1	6.0	

The values of u_r in the formula (3) may change in time therefore it is necessary to ensure the QA/QC. Usually it involves the control of the retention time, repeatability and accuracy of the analyte recovery. QA/QC is performed using a multiple analysis of model gas mixtures with known analytes concentrations, the analysis involves known statistical criteria [38] to evaluate the discrepancy of the established and table values of the tested criteria.

Comparison of the proposed method with the literature data

The proposed methodology allows lower detection limits of alcohols in the air without compromising the metrological characteristics (Table 4).

Table 4. The comparison of GC-FID methodologies of alcohols detection in the air with the preliminary analyte concentration, where TD - thermal desorption, WD - water desorption, ** - the proposed method.

Analyte	Concentration	Concentration	LOD, µg/m ³	RSD, %	Literature
	Method	Time, min			
Methanol	SPE – TD	4	2	6,5	**
	SPE – TD	2	10	5,4	[39]
	SPE – TD	16	4	10	[40]
	SPE – WD	10	11	-	[41]
	Absorb. H ₂ O	10	30	4,3	[42]

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Ethanol	SPE – TD	6	1	5,8	**
	SPE – TD	3	3	4,6	[39]
	SPE – TD	16	3	10	[40]
	SPE – WD	10	10	-	[41]
	Absorb. H ₂ O	10	40	5,3	[42]

Conclusion

In this work we proposed a new high-performance KF-based moisture trapping agent for gas chromatography to selectively remove water from the moist analyzed air without retaining low molecular weight polar organic compounds. Moisture removing agent allows several times increase in breakthrough volumes for low molecular weight VOC. Sequential trapping system was applied for concentration of low molecular weight alcohols and ketones from the humid air resulting in lower detection limits for these substances. Purging of the analyzed air through two traps was conducted in sequence where first trap was filled with KF-based moisture trapping agent and another trap was filled with activated charcoal to retain the low weight alcohols and ketones. The proposed trapping assembly allows determining the lower molecular weight VOC at the levels of μ g/m3 with RSD not exceeding 5 % after 4-8 minutes of preconcentration.

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