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Sorbents based on transition metal salts for the retention of low molecular weight N-, O- and S-containing organic compounds from the air flow

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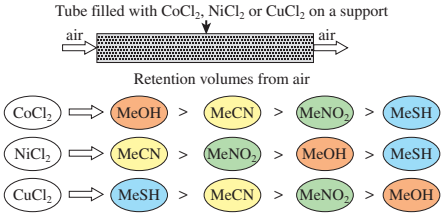
Regularities for the retention of low molecular weight N-, O- and S-containing organic compounds from the air flow have been established for the sorbents based on transition metal (Ni^{II}, Co^{II}, and Cu^{II}) chlorides. The performance of developed sorbents was compared with that of some commercially available materials.



Volatile organic compounds (VOCs) may cause tangible detrimental effects on the human health and environment, since most of them are toxic and/or cancer-inducing.[1] To determine the content of organic compounds in the air, a stage of pre-concentration is usually required. In addition, the development of efficient sorbents for the air purification from VOCs is also a crucial problem. Carbon adsorbents,[2–4] nanotubes[5] and graphene[6] are favored for a pre-concentration of low-molecular weight VOCs. However, all the known sorbents, including carbon molecular sieves[†] and stationary liquid phases, do not procure effective retention of such organic compounds.[7] There are no ways to separate compounds with regard to their polarity. Virtually, there are no reported sorbents capable of selective retaining polar organic compounds containing different heteroatoms.

To this end, one could employ sorbents based on transition metal salts, which were initially proposed for the gas-chromatographic separation of low-molecular weight oxygen-containing organic compounds.[8] Proposed composite sorbents, so-called 'salt in a porous matrix' are characterized by a high intensity of dipole–dipole and donor–acceptor interaction with molecules of polar compounds, which allows them to be applied for the accumulation and conversion of thermal energy.[9] Meanwhile, capabilities of suchlike sorbents for the sorption retention have not been fully unveiled yet. We have previously proposed sorbents based on inorganic salts exhibiting a high adsorptive affinity towards low alcohols and ketones, *i.e.* towards the oxygen-containing VOCs.[10–12] The maximum of such an affinity was observed in the case of cobalt chloride, the nature of anion being of secondary significance. However, an opportunity to retain nitrogen- and sulfur-containing VOCs is still remaining unexplored.

It is commonly accepted that various transition metals possess a different affinity towards N, O and S atoms. All the cations can be subdivided into several groups by their affinity towards the complex formation.[13,14] One of such groups embraces ions of metals, whose electronic structure is close to that of inert gases possessing a small number of *d*-electrons. Ions of this group, *e.g.* Co^{II} and Mg^{II}, form a more stable bond with oxygen as compared to that with nitrogen. Another group is represented by ions containing the complete *d*-electron level and a large number of *d*-electrons. These ions (Ni^{II} and Cu^{II}) form a more stable coordination bond with the N atom as compared to that with oxygen atom. The Cu^{II} ions are also distinguished by their high affinity for S atoms.

Manifestations of similar trends may be well anticipated in the framework of the hard and soft acids and bases (HSAB) theory.[15] According to this theory, the hard acids demonstrate the higher affinity regarding hard bases, while the soft ones – towards the soft bases. Although all of the Co^{2+}, Ni^{2+} and Cu^{2+} cations are the acids of medium hardness, their hardness decreases in the indicated succession. On the other hand, alcohols are the hard bases, mercaptans are the soft bases, while nitriles and pyridine exhibit an intermediate hardness. Therefore, one may expect a greater affinity of cobalt as a more hard acid to alcohols, and that of copper towards the mercaptans.

Obviously, the cited taxonomy appears as an over-simplifying one, insofar as affinity of heteroatoms in the organic substances towards particular transition metals is substantively dependent on the nature of heteroatom milieu in an organic molecule.[16] Despite a salient progress in the *a priori* model predictions regarding trends of interactions of organic molecules containing heteroatoms with compounds of various transition metals,[17] the development of selective sorbents based on these metals to the end of retention of VOC is still an issue of the current concern.[18]

Thus, the present work was aimed at the experimental establishment of regularities for the retention of VOCs containing various heteroatoms (N, O, and S) by sorbents based on chlorides of transition metals (Co, Ni, and Cu) and at the verification of principal possibility of designing sorbents retaining selectively similar VOCs.[‡]

[†] According to ISO16017-1:2000, Indoor, ambient and workplace air. Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography. Part 1: Pumped sampling (IDT).

[‡] To enhance the specific area of compositional stationary phase, the starting non-porous salts were spread over a macro-porous diatomite support Porochrom-III (Supelco, Inc.). A sample of the salt ($CoCl_2$, $NiCl_2$ or $CuCl_2$), preliminary dehydrated by heating, was dissolved in distilled water, thereafter a weighed amount of the support was added to

The salt quantity on the support was determined from an increase in the sorbent mass after its sifting for the separation from the non-immobilized salt. Tubes of the inner diameter of 3 mm and length of 5 cm were filled with prepared sorbents. The processed sorbents were compared with the most efficient and commercially available alternatives.[§]

The flow of a model gas mixture (MGM) containing the tested VOCs at the constant concentration was directed into a tube filled with the sorbent, while the gas outflow from the tube was fed into a sampling loop (1 cm^3) of a heated sampling valve. The selection and injection of sample into a chromatograph were periodically performed. The MGM flow rate was 100 ml min^{-1}. The chroatographic peak heights of analytes at the outflow of tube (h) were compared with the peak heights obtained by the injection of MGM into the tube (h_0). Spanning the domain of linear reciprocity of the detector signal *vs*. concentration of an analyte, the ratio h/h_0 equals to the value of C/C_0, where C and C_0 are the concentrations of analyte at the outlet and inlet of sorption tube, respectively. The retention curves for the test compounds were then plotted as dependences of the C/C_0 ratio against V, where V is the MGM volume, which passed through the tube. These dependences provided the breakthrough (V_B) and retention (V_R) volumes, which were set equal to the values that correspond to $C/C_0 = 0.05$ and $C/C_0 = 0.5$, respectively. Figure 1 shows a typical output of MeOH vapor retention on a column packed with $CoCl_2$.

Experimentally determined V_R values for N-, O- and S-containing VOCs (Table 1) confirmed our assumption that $NiCl_2$ possesses the greater affinity towards N-containing compounds (MeCN, $MeNO_2$, and pyridine) as compared to $CuCl_2$ and $CoCl_2$. The O-containing VOCs (alcohols and ketones) were better retained by $CoCl_2$ relative to other salts tried. Sorbents based on $CuCl_2$ demonstrated the high selectivity towards S-containing compounds. The acquired results comply well with the mentioned HSAB principle, *viz*., mercaptans as the soft bases are stronger retained by Cu^{II}-based sorbents, while alcohols being the hard bases demonstrated the higher affinity towards the Co^{II} sorbents.

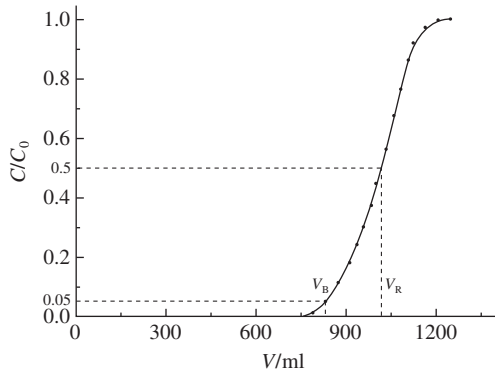


Figure 1 The output curve of methanol retention by the sorbent based on $CoCl_2$ (20 wt% on Porochrom-III).

Table 1 Specific retention volumes (T = 293.2 K) for N-, O- and S-containing organic compounds obtained using the sorbents containing various salts (20 wt% on Porochrom-III).

Test compound	Specific retention volume/dm^3 g^{-1}				
	$CuCl_2$	$CoCl_2$	$NiCl_2$	Chromosorb 106	Tenax TA
MeCN	3.90±0.15	6.4±0.3	23.0±0.8	4.2±0.3	1.3±0.1
$MeNO_2$	1.20±0.06	1.00±0.04	13.0±0.5	5.4±0.3	1.8±0.2
Pyridine	0.80±0.04	1.80±0.06	8.5±0.3	–	4.2±0.3
MeOH	1.10±0.05	17.0±0.6	12.0±0.5	1.1±0.1	<0.3
EtOH	1.20±0.05	21.0±0.7	16.0±0.6	3.6±0.3	1.1±0.1
Acetone	4.3±0.2	12.0±0.4	14.0±0.6	3.9±0.2	0.95±0.07
Methyl ethyl ketone	6.30±0.25	20.0±0.8	15.0±0.6	12.3±1.1	2.9±0.21
H_2S	660±30	<1	<1	<1	<0.3
MeSH	700±35	<1	<1	22±1	5.7±0.3
EtSH	845±45	<1	<1	59±4	18.3±0.9

Properties of the studied sorbents were compared with those of some materials recommended for the gas adsorptive preconcentration in the analysis of air. Specific V_B values were determined for the following adsorbents: a polymer adsorbent Tenax TA, which is superior due to its high thermal stability; a polymer adsorbent Chromosorb 106 possessing an extremely high specific area (800 m^2 g^{-1}); carbon molecular sieve Carboxen 1000; and activated carbons of various brands (Table 2). Admittedly, the high affinity of active charcoals towards organic compounds often impedes thermal desorption of the latter, which necessitates using the sorbents with a lesser specific area, *e.g.*, Tenax.[19] The sorbents based on $CoCl_2$ and $CuCl_2$ surpass some of the charcoals in the case of MeOH and MeSH. The high thermal stability of developed sorbents along with their high affinity towards polar organic compounds containing various heteroatoms make them promising for the adsorptive retention of mentioned VOCs.

Since the salts used as sorbents form crystallohydrates, an increase in the air humidity causes a decrease in the retention parameters of VOC.[12] However, it is worth to note that the heating of sorbents at 300 °C under a flow of dry air completely recovers their adsorptive properties. It pertains to all of the sorbents and test compounds, except for sulfur compounds. Presumably, the latter ones may chemically react in the presence of water vapors with Cu^{II} cations thus producing sulfides.

In conclusion, the regularities concerning retention of similar N-, O- and S-containing volatile organic compounds from the air

Table 2 Specific V_B values (T = 293.2 K) for polar organic compounds obtained using various sorbents.

Sorbent	Specific breakthrough volume/dm^3 g^{-1}				
	MeOH	Me_2CO	MeCN	$MeNO_2$	MeSH
Active charcoal BAU	8.5±0.4	52±2	29±1	38±2	490±20
Active charcoal SKT	14.0±0.6	65±3	22±1	36±2	–
Active charcoal FAS	24±1	115±5	48±2	64±3	–
Carboxen 1000	27±1	125±5	51±2	61±3	–
Tenax TA	< 0.3	0.8±0.1	1.0±0.1	1.4±0.2	4.3±0.3
Chromosorb 106	0.7±0.1	3.1±0.2	3.4±0.3	4.7±0.3	17±1
MCl_2 (20 wt%)[a] on Porochrom-III	10.0±0.5 (Co)	11.0±0.4 (Co)	21.0±0.6 (Ni)	9.5±0.4 (Ni)	560±25 (Cu)

[a] M denotes the transition metal used.

the solution. The resulting mixture was boiled out to a friable state, which underwent drying in a baker at 280 °C until attaining a constant mass. Surface areas and porosity of the sorbents were measured with automated system ASAP *via* adsorption of Kr according to the BET methodology. Krypton was chosen due to a moderate specific area of the sorbents. The coating of Porochrom-III with transition metal salts results in an insignificant (within margin of 10–15%) decrease of the sorbent specific area and porosity, thus maintaining uniform filling of pores inside the support by sufficiently small crystals of the salt.

[§] Tenax TA (Supelco, Inc.), carbon molecular sieves Carboxen 1000 (Supelco, Inc.), Chromosorb 106, and activated carbons: a birch-tree activated charcoal BAC (Supelco, Inc.), SKT and carbon sorbent FAS based on thermoplastic polymers (NPO Neoorganica, Russia) with the particle sizes of 0.25–0.5 mm were used as the reference sorbents. They were placed in the tubes of the same size.

Regularities of retention of organic compounds from the gaseous phase by the studied sorbents were investigated using a Crystal 5000.2 gas chromatograph equipped with a flame-ionization detector for N-, O-containing compounds and with a flame-photometric detector for S-containing ones.

flow by sorbents based on Ni^{II}, Co^{II} and Cu^{II} chlorides have been established. The higher affinities revealed are as follows: for $NiCl_2$ towards N-containing compounds (MeCN, $MeNO_2$, and pyridine), for $CoCl_2$ towards O-containing ones (lower alcohols and ketones), and for $CuCl_2$ towards S-containing compounds (mercaptans and H_2S). The observed trends are in a well agreement with the HSAB theory.

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References

1 X. Zhang, B. Gao, A. E. Creamer, C. Cao and Y. Li, *J. Hazard. Mater*., 2017, **338**, 102.
2 A. Andrade-Eiroa, M. Canle, V. Leroy-Cancellieri and V. Cerdà, *TrAC, Trends Anal. Chem*., 2016, **80**, 641.
3 V. N. Postnov, O. V. Rodinkov, L. N. Moskvin, A. G. Novikov, A. S. Bugaichenko and O. A. Krokhina, *Russ. Chem. Rev*., 2016, **85**, 115.
4 V. N. Postnov, Ya. V. Peretrukhin and A. G. Novikov, *Russ. J. Appl. Chem*., 2013, **86**, 662 (*Zh. Prikl. Khim*., 2013, **86**, 715).
5 A. V. Herrera-Herrera, M. Á. González-Curbelo, J. Hernández-Borges and M. Á. Rodríguez-Delgado, *Anal. Chim. Acta*, 2012, **734**, 1.
6 R. Sitko, B. Zawisza and E. Malicka, *TrAC, Trends Anal. Chem*., 2013, **51**, 33.
7 K. Ciążyńska-Halarewicz, M. Helbin, P. Korzenecki and T. Kowalska, *J. Chromatogr. Sci*., 2007, **45**, 492.
8 L. D. Belyakova, A. M. Kalpakian and A. V. Kiselev, *Chromatographia*, 1974, **7**, 14.
9 Y. Y. Tanashev, A.V. Krajnov and Y. I. Aristov, *Appl. Therm. Eng*., 2013, **61**, 401.
10 O. V. Rodinkov, G. A. Zhuravleva, A. A. Maslyakova, M. V. Petrova and L. N. Moskvin, *J. Anal. Chem*., 2014, **69**, 347 (*Zh. Anal. Khim*., 2014, **69**, 390).
11 O. V. Rodinkov, G. A. Zhuravleva, A. S. Bugaichenko, M. I. Viktorova, V. N. Postnov and A. G. Novikov, *Talanta*, 2015, **144**, 427.
12 O. V. Rodinkov, G. A. Zhuravlyova, E. A. Vaskova and I. A. Platonov, *Anal. Methods*, 2015, **7**, 458.
13 H. S. Taylor, *J. Chem. Educ*., 1928, **5**, 373.
14 N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Clarendon Press, Oxford, 1950.
15 R. G. Pearson, *J. Chem. Sci*., 2005, **117**, 369.
16 G. Frenking and N. Fröhlich, *Chem. Rev*., 2000, **100**, 717.
17 D. H. Nies, *Metallomics*, 2016, **8**, 481.
18 M. Kunaseth, P. Poldorn, A. Junkeaw, J. Meeprasert, C. Rungnim, S. Namuangruk, N. Kungwan, C. Inntam and S. Jungsuttiwong, *Appl. Surface Sci*., 2017, **396**, 1712.
19 E. Gallego, F. J. Roca and J. F. Perales and X. Guardino, *Talanta*, 2010, **81**, 916.

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