

Improvement of activated carbon for air sampling

JAN RUDLING

National Institute of Occupational Health, 171 84 Solna (Sweden)

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SUMMARY

In order to improve the charcoal tube method, activated carbon was treated with benzyl chloride (5 and 20%) in methylene chloride and heated (300°C). The carbons were evaluated with regards to water uptake, adsorption of toluene and carbon tetrachloride, desorption characteristics for polar compounds and storage stability of ketones. Carbons treated with benzyl chloride picked up less moisture, showed higher desorption efficiencies for polar compounds and lower catalytic activity compared with untreated carbons and those heat-treated with helium at 800°C. The best results were obtained with 20% benzyl chloride.

INTRODUCTION

The charcoal tube method^{1,2} has for many years been the standard method for the determination of solvent vapours in workplace air. The method is easy to use and, for many industrial hygiene applications, the sensitivity of liquid desorption is sufficient. However, there are factors that limit the general applicability of the method. In humid atmospheres, water vapour is adsorbed and this often significantly reduces the capacity of the carbon for volatile vapours³. Adsorbed water also influences the desorption efficiency (recovery) for polar compounds⁴. Carbon disulphide (CS₂) is a powerful desorbing agent for non-polar compounds, having a low response on a flame ionization detector and short retention time on most gas chromatographic (GC) columns. However, CS₂ does not give quantitative recoveries for many polar compounds^{5,6}. Moreover, the desorption efficiency (DE) depends on the sample load and the ratio of carbon to desorbing agent. Even though it is possible to overcome this problem by the use of polar solvents, *e.g.*, dimethylformamide⁵, or additions to CS₂ such as alcohols, chromatographic problems due to peak overlap can arise. Another problem with activated carbon is decomposition of the sample (especially for ketones) during storage due to catalytic action or chemisorption⁷.

Although the charcoal tube method is being challenged by other, more sensitive techniques employing "weak adsorbents" such as Tenax⁸ and graphitized carbon black⁹ followed by thermal desorption, the advantage of using activated carbon is that it has a superior sampling capacity, particularly for volatile vapours. A method

that is to be used routinely should allow the collection of samples over several hours at a sampling rate that can be achieved with ordinary sampling equipment. A conclusion from our previous studies¹⁰ was that a possible way to improve the charcoal tube method could be to improve the carbon itself. The carbon commonly used, SKC 120, and other carbons, are probably not the optimum choice.

Activated carbons originating from less well defined sources such as peat, wood and coal often contains mineral impurities (metal oxides), generally referred to as ash and oxygen complexes (surface oxides⁴), that constitute the polar sites of the carbon. To decrease the water uptake of the carbon and to raise the DE for polar compounds, these impurities should be removed. An efficient method to reduce the ash content is leaching with hydrofluoric and hydrochloric acid¹¹. A common way to eliminate many oxygen complexes is heat treatment of the carbon with inert gases¹² or hydrogen^{13,14} at 600–1000°C.

At our institution, we have evaluated a number of activated carbons and treatment procedures¹⁵. Seventeen untreated carbons were tested and the best results were obtained with Sorbonorit 3. The procedures studied were acid leaching, heat treatment with reactive gases (air, carbon dioxide, chlorine and hydrogen) and inert gases (helium and nitrogen at 800 and 1000°C). We found that that the most efficient procedure was acid leaching followed by heat treatment with helium or a mixture of helium and hydrogen at 800°C for a period exceeding 10 h.

Another approach to make a carbon more homogenous is the deposition of pyrolytic carbon on the surface. This can be done with, *e.g.*, methylene chloride¹⁶ and benzene¹⁷. In a prestudy, we recently found that benzyl chloride in methylene chloride could be used and that 300°C was a useful temperature for this treatment. To eliminate impurities (mostly polyaromatic hydrocarbons) formed in this process, desorption at 500°C was carried out.

The purpose of this study was to evaluate two carbons (based on Sorbonorit 3) treated with benzyl chloride and to compare them with (i) Sorbonorit 3, (ii) SKC 120, which is the most commonly used carbon, (iii) helium-treated Sorbonorit 3, which yielded the best result in a previous study¹⁵, and (iv) Carboxen, a modern carbon prepared from a well defined polymer, porous beads of polystyrene–divinylbenzene.

EXPERIMENTAL

Description of carbons

Three carbons purchased in bulk were used, SKC 120 (SKC, Eighty-Four, PA, U.S.A.), Sorbonorit 3 (Norit, Amersfoort, The Netherlands) and Carboxen 563 (Supelco, Bellefonte, PA, U.S.A.). Sorbonorit 3 was crushed and sieved to the same fraction (20–40 mesh) as the other carbons. Before use, untreated SKC and Sorbonorit 3 were dried at 100°C until constant weight.

Treatments

Acid treatment was effected by leaching the carbons (1 g per 10 ml of solution) with 15% hydrofluoric acid (1 day) and 4 M hydrochloric acid (1 day). The carbons were thoroughly rinsed with distilled water until the chloride ions had been removed (pH about neutral) and dried at 100°C.

Benzyl chloride treatment was performed in an erlenmeyer flask by soaking the

carbon (7–8 g) with 25 ml of benzyl chloride (5 and 20%) dissolved in methylene chloride. After 2 days, the methylene chloride was evaporated and the carbon residue was transferred to a furnace. The carbon was conditioned 1.5 h at room temperature before heat treatment (1 l/min nitrogen for 5 h at 300°C followed by 3 h at 500°C).

For thermal treatment a tube furnace was used. The heated zone was *ca.* 30 cm and the sample (7–8 g) was spread out in the centre (about 15 cm) of a quartz tube (diameter 35 mm). Gases were added from a cylinder and the flow-rate was controlled with a rotometer. The heating rate up to the final temperature was 10°C/min. Samples were cooled in an inert atmosphere until a temperature below 100°C was reached. The helium treatment was carried out at 800°C for 20 h (0.5 l/min), preceded by conditioning for 0.5 h at room temperature and 1 h at 200°C.

Treatments of the carbons are summarized in Table I.

Uptake of water

The water uptake was determined by static measurements. Saturated salt solutions giving a constant relative humidity (RH) were placed in 100-ml erlenmeyer flasks and the carbon (50–60 mg) was contained in a threaded basket that was attached to the rubber stopper of the flask. After equilibration for 2 days, the weight increase was recorded and recalculated as microlitres of water per gram of carbon

Uptake of toluene and carbon tetrachloride

Solutions of 0.36 mole fraction of toluene and carbon tetrachloride in hexadecane were used to generate vapours with a relative vapour pressure (vapour pressure/saturated vapour pressure) of 0.36. The solution, contained in a beaker, was placed in the bottom of a vacuum desiccator. The carbon (100 mg), contained in small cups, was weighed and placed in the desiccator. After evacuation and 2 days of equilibration, the weight gain was recorded and recalculated as microlitres of liquid per gram of carbon.

Desorption experiments

Samples (duplicates) were prepared by charging 100 mg of carbon in 3-ml screw-cap vials. The analyte was added to the carbon with a microlitre syringe. Samples were set aside for 1 day (20°C) before desorption and analysis. When the added

TABLE I
TREATMENT OF CARBONS

<i>Designation of carbon^a</i>	<i>Treatment^b</i>
SKC	Conditioned at 100°C before use
Cx	None
Sn	Conditioned at 100°C before use
Sn He	AT + helium 800°C for 20 h
Sn Bc-5%	AT + 5% Bc, 300°C for 5 h + 500°C for 3 h
Sn Bc-20%	AT + 20% Bc, 300°C for 5 h + 500°C for 3 h

^a SKC = SKC 120; Cx = Carboxen 563; Sn = Sorbonorit 3.

^b AT = acid treatment; Bc = benzyl chloride.

amount was 1 μl or less, samples were prepared as mixtures with hexane. The coefficient of variation for these experiments was *ca.* 2% (ref. 10).

Humidified carbon was prepared by the use of saturated salt solutions as described above. The sample addition was then made to the wet carbon.

Samples were desorbed with 1.0 ml of desorbing agent and shaken for a minimum of 1 h. Analyses were made with a Varian 3400 gas chromatograph equipped with a flame ionization detector with the use of standard techniques.

RESULTS AND DISCUSSION

Adsorption of carbon tetrachloride and toluene, at a relative vapour pressure of 0.36, was initially determined (Fig. 1). These experiments give an estimate of the maximum capacity of a microporous adsorbent and they also reveal possible "pore discrimination" effects due to the different critical dimensions of carbon tetrachloride (6.4 Å) and toluene (3.7 Å)¹⁸.

Compared with SKC, the adsorption capacity of untreated Sorbonorit 3 is higher. There is almost no change in capacity after the helium heat treatment (Sn He). Heat treatment removes oxygen but, on the other hand, also decreases the pore diameters. A significant decrease in capacity (carbon tetrachloride) is seen for the carbons treated with benzyl chloride. Deposition of carbon and reactions with surface groups are possible explanations. However, compared with Carboxen, the capacities of the treated carbons are still high.

Adsorption of water vapour was determined at six levels between 45 and 90% RH. These results are presented in Fig. 2. There is a significant difference in the water adsorption pattern between the untreated carbons. SKC shows a poor performance; its water uptake is high at the lowest RH levels (45 and 56%), in contrast to the other carbons. For the Sorbonorit carbon, there is a sharp rise in water uptake between 56 and 66% RH. Helium treatment did not improve this carbon. In fact, there is a

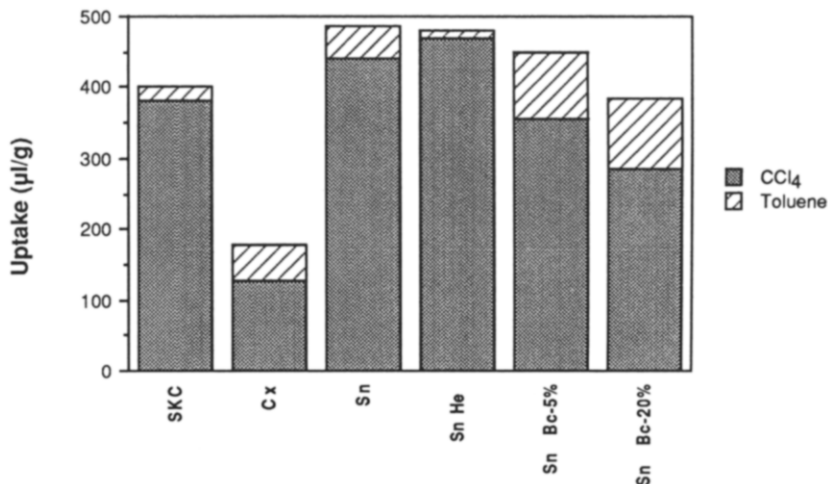


Fig. 1. Adsorption of carbon tetrachloride and toluene at a relative vapour pressure of 0.36. Results given as adsorbed volume (liquid) per gram of carbon.

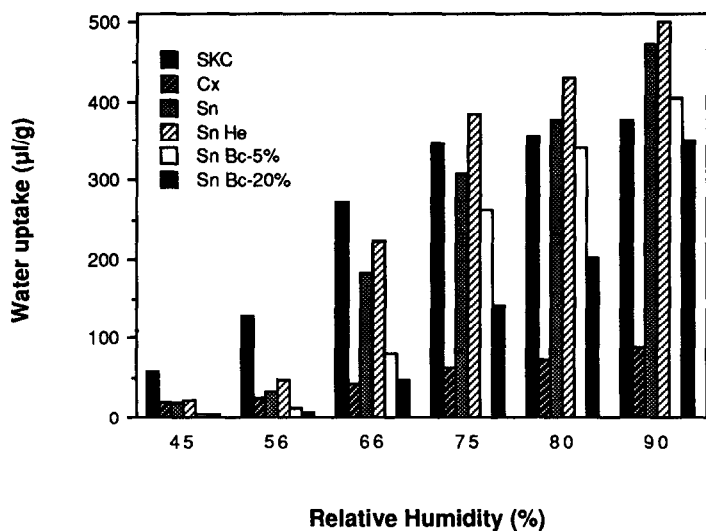


Fig. 2. Uptake of water in microlitres per gram of carbon at different levels of relative humidity.

tendency for increased water uptake that is probably due to a change in the pore structure. The benzyl chloride treatment causes a favourable shift in the water adsorption pattern, especially for the carbon that was treated with a 20% solution (Sn Bc-20%). In this instance, the drastic increase in water uptake commences above 70% RH. Carboxen shows excellent water adsorption characteristics; even at 90% RH the water uptake is small compared with its pore volume.

In a previous study on two carbons (SKC and Merck), we found that the DE for 2-ethoxyethanol (ethyl cellosolve) was extremely dependent on the sample load, whereas for butanol this dependence was not so pronounced¹⁹. Therefore, to evaluate the desorption characteristics for polar compounds, two test series with various amounts of butanol and 2-ethoxyethanol were examined using carbon disulphide as desorbing agent (Tables II and III).

TABLE II

DESORPTION EFFICIENCIES FOR BUTANOL

Experiments (duplicates) made with various amounts of butanol adsorbed on 100 mg of carbon. Desorption made with 1.0 ml of carbon disulphide. DE denotes desorption efficiency.

Carbon	DE (%) for added amount (µl) of butanol					
	0.03	0.10	0.30	1.0	3.0	10
SKC	50	54	57	65	75	80
Cx	64	69	75	78	84	93
Sn	73	77	82	90	95	98
Sn He	83	88	93	95	98	101
Sn Bc-5%	83	89	94	95	96	98
Sn Bc-20%	89	92	95	96	96	100

TABLE III
DESORPTION EFFICIENCIES FOR 2-ETHOXYETHANOL

Experiments (duplicates) made with various amounts of 2-ethoxyethanol adsorbed on 100 mg of carbon. Desorption made with 1.0 ml of carbon disulphide. DE denotes desorption efficiency.

Carbon	<i>DE (%) for added amount (μl) of 2-ethoxyethanol</i>				
	<i>0.1</i>	<i>0.3</i>	<i>1</i>	<i>3</i>	<i>10</i>
SKC	<10	15	33	62	77
Cx	60	63	72	88	91
Sn	48	69	86	94	97
Sn He	78	88	93	97	99
Sn Bc-5%	84	93	97	95	100
Sn Bc-20%	86	93	96	98	99

It is clear that Sorbonorit 3 shows better results than SKC. For both carbons, the DEs for butanol are higher than those of 2-ethoxyethanol (corresponding amounts). For Carboxen, the recoveries (lower range) are also far from quantitative. The effect of the treatments is obvious. Helium treatment, which decreases the amount of oxygen complexes, renders the surface more hydrophobic, which results in a significant improvement in the DE in the lower sample range. The benzyl chloride treatment means a further improvement in the desorption characteristics of the carbon. The variations in DE with sample load for Sn Bc-20% are rather small, and linearity in DE is approached.

A serious problem with solvent desorption when a non-polar solvent such as carbon disulphide is used, is the impact of water on the DE of polar compounds⁴. To study the influence of water, tests were made with a mixture of 0.5 μ l of butanol and 0.5 μ l of 2-ethoxyethanol added to dry carbon and to carbons previously saturated with water vapour at 60 and 75% RH. The results were compared and the RH level giving a decrease in DE of 10% was calculated (Table IV). As expected from previous work⁴, the water uptake pattern (Fig. 1) is reflected in the results.

TABLE IV
INFLUENCE OF WATER ON DESORPTION EFFICIENCY

Calculation of RH level that causes the desorption efficiency to decrease by 10% compared with the desorption efficiency for dry carbon. Experiments (duplicates) done with a mixture of 0.5 μ l of butanol and 0.5 μ l of 2-ethoxyethanol adsorbed on 100 mg of dry carbon and carbons saturated with 60 and 75% RH. As desorbing agent 1.0 ml of carbon disulphide was used.

Carbon	<i>Approximate RH (%)</i>	
	<i>Butanol</i>	<i>2-Ethoxyethanol</i>
SKC	50	< 50
Cx	90	75
Sn	60	50
Sn He	60	50
Sn Bc-5%	70	60
Sn Bc-20%	75	65

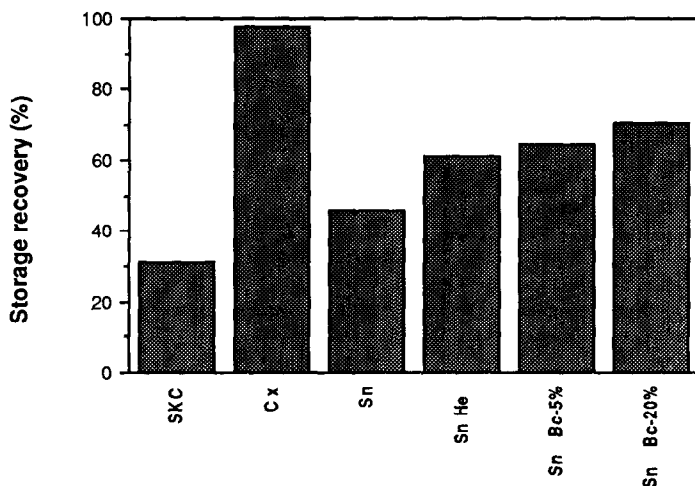


Fig. 3. Recoveries (desorption efficiencies) for samples (duplicates) of cyclohexanone ($3.0 \mu\text{l}$ on 100 mg of carbon) stored for 2 weeks (20°C). Desorption with 1.0 ml of carbon disulphide-acetone (1:1).

To check storage loss of ketones due to chemisorption or catalytic action⁷, storage stability tests (2 weeks at 20°C) with samples of cyclohexanone ($3 \mu\text{l}$ on 100 mg of carbon) were performed. To ensure complete desorption, a mixture of carbon disulphide and acetone was used⁷. The results are presented in Fig. 3. As can be seen, there is no storage loss for Carboxen. Thermal treatment and benzyl chloride treatment reduces the catalytic activity, which is seen as an increase in sample recovery. The test conditions were rough; cold storage is often used to minimize storage losses. When the experiment was repeated with storage for 1 day at room temperature followed by 2 weeks at 0°C ; the sample recoveries for the treated carbons exceeded 90%.

As a conclusion, it can be stated that the treatment with benzyl chloride improves activated carbon in several respects: the water uptake decreases, the DE for polar compounds is significantly increased and the catalytic activity is reduced. However, a slight reduction in capacity is seen. It also appears that treatment with a 20% solution of benzyl chloride yields better results than that with a 5% solution. If a comparison is made with Carboxen, the carbon Sn Bc-20% has a significantly higher adsorption capacity and DEs for polar compounds whereas its water adsorption characteristics above 70% RH and storage stability for ketones are poorer.

It is believed that further improvements will be possible by using other concentrations of benzyl chloride and treatment conditions. The use of a rotating furnace or fluidized bed is a possibility. Possibly benzyl chloride should be fed as a vapour directly to the carbon contained in a heated furnace.

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