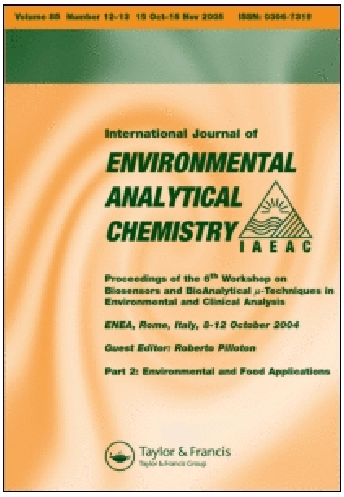

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Adsorbents for the Specific Retention of Basic Organic Nitrogen Compounds

C. S. Giam[a]; Jun-Ichi Itoh[b]; Jack E. Leonard[a]
[a] Department of Cehmistry, texas A&M University, TX [b] Department of Environmental Chemistry, Kitami Institute of Technology, Kitami, Hokkaido, Japan

To cite this Article Giam, C. S. , Itoh, Jun-Ichi and Leonard, Jack E.(1984) 'Adsorbents for the Specific Retention of Basic Organic Nitrogen Compounds', International Journal of Environmental Analytical Chemistry, 16: 4, 285 — 293
To link to this Article: DOI: 10.1080/03067318408076958
URL: http://dx.doi.org/10.1080/03067318408076958

Intern. J. Environ. Anal., Chem., 1984, Vol. 16, pp. 285–293
0306-7319/84/1604-0285 $18.50/50

Printed in Great Britain

Adsorbents for the Specific Retention of Basic Organic Nitrogen Compounds

C. S. GIAM,† JUN-ICHI ITOH,‡ AND JACK E. LEONARD
Department of Chemistry, Texas A&M University, College Station, TX 77843

(*Received August 22, 1983*)

The use of zinc and cobalt tetraphenylporphines and zinc phthalocyanine (adsorbed on graphitized carbon black) for the specific retention of aliphatic, aromatic and heteroaromatic amines was assessed by isothermal gas chromatography. These adsorbents showed a high selectivity for unhindered amines which allowed them to be well separated from acidic and neutral organic compounds and hindered amines. The retention of organics is high at room temperature, but they can be desorbed at higher temperatures. Data on the relative strength of the interaction with a variety of organic compounds are presented.

KEY WORDS: adsorption, amine, gas chromatography, metalloporphyrin, specific retention volume.

INTRODUCTION

Our research group is involved in the analysis of environmental amines and nitrogen heterocycles.[1,2] In the course of this work we have sought to improve the techniques for analyzing complex mixtures of organic compounds in atmospheric samples at trace concentrations. Conventional analytical methods require that the

---

†To whom reprint requests should be addressed.

‡Current address: Department of Environmental Chemistry, Kitami Institute of Technology, Kitami, Hokkaido 090, Japan.

organics be adsorbed on some material (Florisil[2] or polyurethane foam,[3] for example), desorbed with solvent, and then separated from other organics by acid/base extraction. Only then can the final characterization of these basic nitrogen compounds be carried out. The improvement which we sought would reduce this procedure's complexity by combining the adsorption/desorption phase with the chemical separation phase to provide a rapid but efficient separation of amines from other organic contaminants.

Our approach uses metal complexes for the specific retention of nitrogen compounds; such complex formation has been applied to the gas chromatography of other functional groups for decades.[4-6] The particular metal complexes which we chose to work with are porphyrins, namely, the zinc and cobalt complexes of 21H, 23H −5, 10, 15, 20-tetraphenylporphine (H_2TPP; ZnTPP and CoTPP are the complexes) and zinc phthalocyanine (ZnPC). These complexes are good Lewis acids and have an open ligand site,[7-9] so they should have the proper retentivity for our purposes. We report here on our preliminary investigations of the retention of organics on carbon-adsorbed metalloporphyrins which display the desired amine selectivity.

EXPERIMENTAL

Materials

All reagents used were reagent grade or better. Pyrrole and benzaldehyde were redistilled before use. H_2TPP, ZnTPP and CoTPP were prepared by the method of Adler and coworkers.[10,11] Lithium phthalocyanine (Li_2PC) was prepared by adding 30 g phthalonitrile to a solution made by dissolving 2 g of lithium wire in 150 mL hexanol. The solution was refluxed 30 min after the initial exothermic reaction ended. It was cooled, an equal volume of benzene was added, and it was left overnight. The solution was filtered and the crude product washed with benzene until the filtrate was colorless. The solid was dried under vacuum at 215°C for 3 h and then extracted (Soxhlet apparatus) with 150 mL dry acetone for 24 h. The final yield was 19.5 g (67%). The salt was converted to H_2PC and ZnPC using the literature procedure.[12] Spectral data (IR, UV, ^{1}H-NMR) agreed with the literature values. Graphitized thermal carbon black (Alltech Associates Graphpac GC, 80–100 mesh) was pretreated by heating under nitrogen at 350°C.

Gas chromatography

Gas chromatograms were run on a Varian 1700 instrument equipped with a flame ionization detector and a Fisher Recordall 5000 recorder. Gas flow rates were measured at the exit port with a soap bubble flow meter. Retention times were determined by length measurements on the stripchart output and compared to stopwatch determinations of the chart speed. Specific retention volumes (V_g in $mL_{adsorbed}/g_{adsorbent}$) were calculated by Littlewood's method[13] from two or more determinations of the retention time.

Packed columns were prepared by standard methods. For example, ZnTPP/C was prepared by dissolving the porphyrin (0.225 g) in a minimal volume (about 25 mL) of hot dimethylformamide and adding 4.5 g Graphpac GC. The resulting suspension was cooled and an equal volume of water was added. After ten minutes the suspension was filtered, washed with water and dried at 130°C. About three grams of this material (5% w/w) was packed with slight vibration into a 1/8″ × 1-*m* stainless steel column. The column was conditioned overnight at 200°C under nitrogen flow. Other columns were prepared using CoTPP, H_2TPP, and using other support materials such as silica (Porasil A), diatomaceous earth (Gas Chrom Q) and Florisil. We also used pure ZnTPP as an adsorbent. The crystalline solid was pelletized in a standard laboratory press used for preparing KBr pellets in IR analysis. The pellets were ground, sieved to produce an 80/100 mesh fraction, and packed into a chromatography column.

RESULTS

These experiments were designed to survey potential adsorbents by gas chromatography to find ones which would strongly and selectively retain the desired compounds (i.e., amines and nitrogen heterocycles) at or near room temperature and then release them at an elevated temperature. We chose the porphyrin derivatives

(ZnTPP, CoTPP and ZnPC) because they are highly stable and interact strongly with a variety of basic organic nitrogen compounds.

We initially tried pure ZnTPP as an adsorbent. We pelletized the solid and prepared an 80/100 mesh gas chromatograph column packing from it, but it was much too retentive: nitrogenous bases were totally retained even at 200°C. In subsequent experiments we reduced the retentivity of the complex by dilution on various supports. Supports used included silica (Porasil A), diatomaceous earth (Gas Chrom Q), and Florisil. None of these supports was suitable. There was little difference in retention order or specific retention volumes between H_2TPP on Porasil A and ZnTPP on the same support. Attempts at coating Gas Chrom Q with porphyrin derivatives produced columns with little retention except at very low temperatures. Columns prepared with Florisil retained all polar compounds at temperatures up to 300°C. Our experiments using graphitized thermal carbon black (Graphpac GC) provided a stable, high surface area support that held the macrocyclic compounds (ZnPC, ZnTPP, CoTPP and H_2TPP) well. The high temperature limit for desorption of compounds from the ZnTPP/C adsorbent is set by the sublimation of the complex at about 280°C. We used 220°C as the working temperature limit for all three metalloporphyrin adsorbents in this work.

The carbon black-supported metalloporphyrin columns show an interesting and unusual pattern of retention volumes for different columns. Kiselev and his coworkers[14-16] have reported the chromatographic properties of thermalized carbon black itself. They have established that the best predictor of retention order on such columns is molecular polarizability; steric effects are a minor second predictor. Thus, they observed that benzene is held about as strongly as pyridine, and toluene is retained about as well as 2-methylpyridine (Table I).

The mechanism of adsorption on carbon-supported ZnTPP is very different. Where basic nitrogens are present in the molecule, it is held much more strongly than comparable nonbasic compounds. Thus, pyridine is held more strongly than any of the hydrocarbons or neutral organics (Table II). Steric effects are very important on this adsorbent; the stronger but more hindered amines such as triethylamine, 2-methylpyridine and 2,6-dimethylpyridine have much smaller retention than expected from basicity alone. Compounds

TABLE I

Retention of organic compounds on graphitized carbon black at 150°C.[a]

Compound	V_s	ln V_g
aniline	2.74	3.04
N,*N*-dimethylaniline	39.8	5.71
pyridine	0.47	1.27
2-methylpyridine	3.00	3.17
3-methylpyridine	3.10	3.16
hexane	0.63	1.57
n-octane	6.02	3.82
benzene	0.41	1.14
toluene	1.65	2.53
ethanol	0.05	−0.97
acetone	0.06	−0.79
acetic acid	0.16	0.20

[a] Source: Ref. 15. V_s is the retention volume per unit surface area; ln V_g is the natural logarithm of the retention volume per unit mass of adsorbent calculated from Kiselev's data using the stated value of 7.6 m^2/g in Ref. 15. The original data have been recalculated to facilitate comparison with the values in Tables II and III.

TABLE II

Specific retention volumes of compounds chromatographed on H_2TPP/C and ZnTPP/C.

	ln V_g	
Compound	5% H_2TPP/C	5% ZnTPP/C
Nitrogen bases		
propylamine	2.35	4.03
pyridine	2.93	4.24[a]
2-methylpyridine	2.76	2.77[a]
aniline	3.08	3.94[a]
Other organics		
hexane	0.89	1.06
isooctane	2.56	2.72
benzene	0.65	1.38
toluene	1.84	2.37
ethanol	0.14	0.68
acetone	−0.36	0.17

[a] These values were measured at 160°C; all others are for 120°C. The amines are so strongly retained on the metalloporphyrin column that they do not elute in a reasonable time at the lower temperature, but 160°C is too high a temperature to accurately measure the adsorption of most of the other organics.

which lack basic nitrogen groups do not show any marked differences in relative ordering on the metalloporphyrin columns from what might be expected on the carbon support or on the carbon-supported porphyrin ligand itself (H_2TPP/C).

Following these preliminary studies with ZnTPP/C and H_2TPP/C, a more extensive study was carried out for all three metalloporphyrin adsorbents (CoTPP/C, ZnTPP/C and ZnPC/C). The specific retention volumes were calculated from the retention time data in order to use Littlewood's observation that the logarithm of the specific retention volume (V_g, calculated from the retention times) is a linear function of the inverse Kelvin temperature.[17] Since the specific retention volume is related to the equilibrium constant for the gas-solid reaction, this correlation is simply an extension of the van't Hoff relation to the adsorption process. A minimum of three and a maximum of seven temperatures were studied for each of the 28 compounds used. The linearity of the van't Hoff plot was determined using ordinary linear regression analysis. Except for a few compounds (noted in Table III), linearity was observed for all compounds and adsorbents. Table III lists the extrapolated V_g values at 150° for all compounds which had a correlation coefficient above 0.99 ($>90\%$ of the compounds studied). The value of 150° was chosen in order to minimize the amount of extrapolation required, since poorly retained compounds (hydrocarbons, hindered amines, alcohols, etc.) had very short retention times above about 130°C, while the most strongly retained compounds (such as 3,5-dimethylpyridine) could not be removed from the column below about 160°C. Thus, no single temperature could be used for reporting all of the data without extrapolation.

Four generalizations about these adsorbents can be made from these data. (1) At any given temperature there is a wide but predictable variation in the retention times between different compound classes. On all adsorbents there is strong retention of unhindered amines and relatively poor retention of hydrocarbons and oxygen and sulfur compounds. Hindered amines (triethylamine, 2-methylpyridine, 2,6-dimethylpyridine) are poorly retained on all columns, with a larger steric effect observed on the TPP columns than on the ZnPC adsorbent. (2) Adsorbed compounds can be removed by heating the adsorbent. As mentioned, the high temperature limit of 220°C is well below the sublimation limit of the

TABLE III

Specific retention volume of various organic compounds on metalloporphyrin adsorbents at 150°C.

	$\ln V_g$		
Compound	CoTPP	ZnTPP	ZnPC
Alkylamines:			
methylamine	2.203	a	3.309
ethylamine	2.764	3.867	4.343
diethylamine	2.545	4.072	4.879
triethylamine	1.095	1.097	1.626
1-aminopropane	3.314	4.527	4.955
1-aminobutane	3.987	5.333	5.846
Arylamines:			
aniline	3.819	4.341	3.823
N-methylaniline	4.084	4.632	5.199
N,N-dimethylaniline	3.232	3.901	5.171
Pyridines:			
pyridine	3.978[b]	4.731	5.646
2-methylpyridine	2.002	3.055	3.925
4-methylpyridine	4.855	5.720	6.911
2,6-dimethylpyridine	2.085[b]	2.262	1.960
2,5-dimethylpyridine	3.117	4.305	5.534
3,5-dimethylpyridine	6.106	7.325	8.322
Hydrocarbons:			
hexane	0.249[b]	0.203	0.275
hexene	0.249[b]	0.203	0.279
isooctane	1.753[b]	1.686	1.692
benzene	0.253[b]	0.527	0.417
toluene	1.169[b]	1.342	1.532
Miscellaneous:			
nitrobenzene	3.279	3.722	2.808
thiophene	0.136	0.405	a
ethyl sulfide	2.237	1.717	1.799
triethyl phosphite	a	3.895	−0.455
tetrahydrofuran	0.472[b]	1.750	2.258
ethanol	a	−0.245	−0.221
acetone	a	−0.542	0.255
acetic acid	0.989	a	a

[a] The plot of $\ln V_g$ vs $1/T$ is not linear for this compound on this column, so no value is reported.

[b] Experimental value at 150°C; all other values are extrapolated (or interpolated) from a linear $\ln V_g$ vs $1/T$ plot.

complexes, and it was picked so that good resolution of the compounds could still be observed. However, if desired, rapid desorption of the retained compounds could be done at a higher temperature for plug injection into a gas chromatograph. (3) The adsorption behavior of all three metalloporphyrin columns can be correlated. Table IV shows the correlation data obtained from the results in Table III. From the first line it can be seen that ZnPC/C is more retentive than ZnTPP/C; from the second line it is clear that ZnTPP/C has a greater affinity for these compounds than does CoTPP/C. When the ligand effect (PC > TPP) is combined with the metal effect (Zn > Co), the third line shows the expected and observed result (ZnPC/C > CoTPP/C). (4) Each of these adsorbents provides useful properties for environmental analysis, and the adsorbent of choice depends on the particular application. Where maximum resolution is desired (e.g., gas chromatographic use), ZnPC/C is the most generally useful. For applications in which ease of desorption is the main criterion (e.g., concentration of bases from air samples), the less retentive CoTPP/C adsorbent might be preferred.

These results demonstrate that metalloporphyrin columns should be a useful addition to the adsorbents employed in the collection and analysis of complex organic mixtures in atmospheric studies. They are stable, selective and easily prepared.

TABLE IV

Correlation of adsorbent behavior at 150°C for metalloporphyrins adsorbed on carbon.

Adsorbent 1 (x)	Adsorbent 2 (y)	Slope	Intercept	Correlation coefficient	N
ZnPC/C	ZnTPP/C	0.834	0.193	0.974	22
ZnTPP/C	CoTPP/C	0.801	0.057	0.968	23
ZnPC/C	CoTPP/C	0.648	0.232	0.921	23

Acknowledgements

This work was supported by the Robert A. Welch Foundation of Houston, Texas, Grant A-240. Mr. Russell Seguin provided valuable experimental assistance.

References

1. J. E. Leonard, J.-I. Itoh and C. S. Giam, *N. Mex. J. Sci.* **22,** 17 (1982).
2. J. Adams, E. Atlas and C. S. Giam, *Anal. Chem.* **54,** 1515 (1982).
3. C. S. Giam, E. L. Atlas, H. S. Chan, Proc. 4th Jt. Conf. Sensing Environ. Pollut., p. 707, 1977.
4. B. W. Bradford, D. Harvey and D. E. Chalkley, *J. Inst. Petrol.* **41,** 80 (1955).
5. D. W. Barber, C. S. G. Phillips, G. F. Tusa and A. Verdin, *J. Chem. Soc.*, 18 (1979).
6. J. J. Fraken, C. Vidal-Madjar and G. Guiochon, *Anal. Chem.* **43,** 2034 (1971).
7. G. C. Vogel and Lynn A. Searby, *Inorg. Chem.* **12,** 960 (1973).
8. G. C. Vogel and J. R. Stahlbush, *Inorg. Chem.* **16,** 950 (1977).
9. M. Nappa and J. S. Valentine, *J. Amer. Chem. Soc.* **100,** 5075 (1978).
10. A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.* **33,** 476 (1967).
11. A. D. Adler, F. R. Longo, F. Kampus and J. Kim, *J. Inorg. Nucl. Chem.* **32,** 2443 (1970).
12. Vidal-Madjar, C., Guiochon, G., *J. Chromatogr. Sci.* **9,** 664 (1971).
13. A. B. Littlewood, *Gas Chromatography. Principles, Techniques and Applications*, 2nd ed., Academic Press, New York, 1970, esp. ch. 2, 3.
14. E. V. Kalaschnikova, A. V. Kiselev, R. S. Petrova and K. D. Shcherbakova, *Chromatographia* **4,** 495 (1971).
15. A. V. Kiselev, I. A. Migunova and Ya. I. Yashin, *Russ. J. Phys. Chem.*, 4244 (1968).
16. A. V. Kiselev and D. P. Poshkus, *Russ. J. Phys. Chem.* **41,** 1433 (1967).
17. A. B. Littlewood, *Anal. Chem.* **36,** 1441 (1964).