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ION-EXCHANGE PACKING WITH HIGH TEMPERATURE STABILITY FOR GAS-SOLID CHROMATOGRAPHY

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SUMMARY

An ion-exchange packing for use in gas-solid chromatography was prepared with a high temperature stable polymer and characterized in Cu^{2+} form using several aromatic amines. Silica glass beads were coated at 2.2% (w/w) with poly-2,6-diphenyl-*p*-phenylene oxide which was then sulfonated and exchanged using Cu^{2+} . Capacity of the material was determined through titration as 0.16 mequiv./g of packing or 7.4 mequiv./g of polymer. Selectivity of amines *versus* aromatic hydrocarbon analogs was exhibited by the packing in Cu^{2+} form and t'_R increased for aromatic amines: primary > secondary > tertiary. These results are consistent with steric hindrance in group specific interactions such as complexation. Changes in k' for aniline and N,N-dimethylaniline were less than 5-6% for the Cu^{2+} form during a 48-h period with column temperature of 250°C. No shrinkage of the column packing was observed under these conditions. Properties of thermal stability and specificity exhibited by this material are satisfactory for further characterization as a selective adsorbent for amines in atmospheric samples.

INTRODUCTION

Materials which have properties of selective absorption for particular functional groups such as sulfides or amines were prepared during the 1960s for use in liquid-solid chromatography (LSC). These materials commonly were prepared through impregnation of silica with metal compounds including CoO (ref. 1), Raney Co (ref. 2), $\text{Zn}[\text{Fe}(\text{CN})_2]_2$ (ref. 3), and FeCl_3 (ref. 4) for separation of sulfides, sulfonamides, and oxime derivatives respectively. However, except for limited application with metal salts⁵ use of such mechanisms in separation with gas-solid chromatography (GSC) have not been widely accepted. Limitations in GSC have been associated with nonlinear isotherms, strong retention, chemisorption, and variations in batches of the same adsorbent. In 1973, Hirsch *et al.*⁶ introduced synthetic macroreticular ion-exchange resins as materials for group-selective separations. Several features, advantageous for use in GSC, were exhibited by these sulfonated resins which were based on a styrene-divinylbenzene co-polymer. Resins in Ag^+ form were mechanically stable, thermally stable to 150-190°C, and group selective for alkenes.

Furthermore, this selectivity could be modified conveniently through exchange of the Ag^+ with other ions. While peak shape mostly was symmetrical for olefins and other hydrocarbons and plate heights were 0.4 to 0.5 cm, slow mass transfer processes related to diffusion in small pores of the resin were detected as slight tailing in peak shape.

Problems of mass transport were solved through two approaches. First, a bonded-phase resin with a porous silica support was prepared successfully in Ag^+ form and applied in separation of olefins and hydrocarbons⁷. Although resolution and peak shape were improved, the upper temperature limit of 188°C was still relatively low. Second, a porous polymer based on an ethylvinylbenzene-divinylbenzene copolymer was lightly sulfonated through control of reaction temperature and time⁸. This attempt to sulfonate only the surface of the resin bead was successful and tailing was reduced, but limitations in temperature were not investigated and temperatures were kept at or below 230°C. Furthermore, interactions of this ion-exchange material with olefins were strong and temperatures of 230°C were required to elute 2-pentene in less than 4 min using a 13-cm long column.

Although ion exchange resins described above may be desulfonated in reactions with water at 150°C, Emerson *et al.*⁹ have shown that many sulfonate groups are sterically isolated in solid polymer. Thus, temperature limitations due to thermal decomposition of ion-exchange polymers in GSC may be governed largely by instability of the aromatic hydrocarbon matrix and not by desulfonation reactions. One objective of this work was the preparation of an ion-exchange resin using a polymer matrix with higher temperature stability than the ethylvinylbenzene-divinylbenzene copolymers which have an upper temperature limits of only 250°C as the unsulfonated hydrophobic resin. Results are presented here on preparation and characterization of an ion-exchange material based on sulfonation of poly-2,6-diphenyl-*p*-phenylene oxide, a polymer with an upper temperature limit of 350°C¹⁰. Both, thermal stability and selectivity for aromatic amines *versus* benzene, toluene, and ethylbenzene have been determined for such an ion-exchange resin in Cu^{2+} form and are described here.

A second objective of this work was development of a sorbent material which would be selective for amines during collection of atmospheric samples and which could then be analyzed using thermal desorption techniques. During the 1970s, large advances were made in collection and determination of toxic organic compounds in atmospheric environments¹¹⁻¹³. However, aliphatic and aromatic amines and other N-containing compounds are mentioned rarely, even though they have been found in automobile exhausts¹⁴, ambient air¹⁵, and cigarette smoke¹⁶. One possible source of this general lack of detection of amines may be found in sampling procedures which collect all type of organic compounds including more abundant aromatic and aliphatic hydrocarbons which may mask the presence of trace concentrations of amines. However, selective absorption in the sampling step may provide a method for reducing these difficulties and provide more detailed information on amine content of atmospheric and other gaseous samples.

EXPERIMENTAL

Sulfonation of polymer

Two procedures were used for sulfonation of polymer which was purchased as commercially available Tenax-GC (80–100 mesh, Alltech, Deerfield, IL, U.S.A.). First, 3.4 g of porous polymer were heated to 125°C for 60 min in a 250-ml round-bottomed flask (with condensor) with 150 ml of concentrated sulfuric acid (ACS Reagent Grade, Fisher Scientific, Fair Lawn, NJ, U.S.A.). The flask was cooled to room temperature and contents were filtered. The filtered polymer was washed with deionized water, methanol, and air dried using aspirator vacuum. A Perkin-Elmer Model 283B infrared (IR) spectrophotometer was used with KBr pellets of starting material and product to monitor success of sulfonation. Second, 3.2 g of polymer were slowly warmed as above to about 120°C with 120 ml of fuming sulfuric acid (J. T. Baker, Phillipsburg, NJ, U.S.A.) for 60 min, but the total time at 120°C for the reaction was only 5 min. The mixture was poured over ice, isolated as before, and characterized by IR spectrophotometry.

Preparation of packing based on ion-exchange resins

Packing based on an ion-exchange resin was prepared through coating 0.096 g of Tenax-GC in methylene chloride solution on 4.315 g of silanized silica glass beads (Volaspher A-2, Manufacturing Chemists, E. Brunswick, NJ, U.S.A.) using a rotary evaporator. Packing was air dried and then sulfonated with fuming sulfuric acid using conditions of 100°C for 30 min. Reaction mixture was poured over ice, filtered, and washed with distilled water until effluent was constant pH. An ion-exchange column for GSC was prepared using 0.48 g of H⁺ form packing in a 40 cm × 2 mm borosilicate glass column.

Also, ion-exchange material was exchanged to the Cu²⁺ form. A concentrated solution of CuBr₂ (J. T. Baker) was prepared and 20 ml of solution was mixed with about 1.5 g of ion-exchange packing. The mixture was gently stirred for 10 min, filtered, and washed using 50 ml of deionized water. Packing was dried at 100°C and large aggregates of packing material were broken carefully using a glass rod. Without further treatment, 0.545 g of Cu²⁺ form ion-exchange material were packed in a glass column as above.

Characterization of packing material

Titration. Sodium hydroxide solution was freshly standardized using potassium acid phthalate and titrated to a phenolphthalein end-point. Capacity of the resin was determined through titration with this NaOH solution using 0.703 g of packing in H⁺ form in 50 ml of rapidly stirred deionized water. Values were corrected using a blank of 50 ml of deionized water.

Temperature stability. Columns were installed in a Hewlett-Packard Model 5721A gas chromatograph equipped with on-column injection port and flame ionization detector (FID). Initially, temperature stability was measured as column bleed during a temperature program of 40°C to 220°C at 6°C/min. Helium carrier gas flow-rate was 3 l ml/min. Later, temperature stability of the Cu²⁺ form ion-exchange material was monitored using retention behavior for aniline and N,N-dimethylaniline. The column was kept at 250°C for 48 h and periodically temperature was reduced to 100°C for characterization.

Elution analysis. Four packing materials, (1) Cu^{2+} form ion-exchange resin (2) H^+ form ion-exchange resin, (3) silica beads (Volaspher A-2), and (4) 3% OV-17 on 100–120 mesh Chromosorb W (Alltech) were characterized between 90°C and 120°C using elution analysis¹⁴. Values for the capacity ratio (k') and the specific retention volume (V_g) were determined using aniline, N-methylaniline, N,N-dimethylaniline, benzene, toluene, and ethylbenzene. Amines were prepared at 20 $\mu\text{g}/\mu\text{l}$ in benzene and others were prepared at same concentrations in methylene chloride.

Chemical characterization. Carbon and hydrogen analyses were made in duplicate by Guelph Chemical Laboratories (Guelph, Canada). Determination of Cu^{2+} was made by atomic absorption spectrometry using a Varian Techtron Model AA5 following acid digestion of a portion of the resin.

RESULTS AND DISCUSSION

Use of poly-2,6-diphenyl-*p*-phenylene oxide (Tenax-GC) in this study was based on the possibility that decomposition of dry ion-exchange resins is governed kinetically not by desulfonation, but rather by thermal instability of the aromatic hydrocarbon matrix. However, sulfonation of a polymer also may result in reduced thermal stability of this hydrocarbon matrix. Although thermal stability of Tenax-GC is 100°C higher (350°C) than styrene-divinylbenzene polymers (250°C) reports on sulfonation of Tenax-GC were not found. Sulfonation of Tenax-GC was first attempted here using hot (120°C) concentrated sulfuric acid which has been used successfully to sulfonate styrene-divinylbenzene polymers¹⁷. Color and wettability of product from this reaction were identical to those for starting material and IR analysis of recovered product confirmed no reaction occurred. Next, fuming sulfuric acid was used at 120°C for sulfonation. Near 50°C the solution turned light brown and the color of Tenax-GC turned off-white. Polymer was isolated, after the reaction was quenched, as a yellow, gel-like material with a volume (wet) nearly four times the starting volume of Tenax-GC. The washed and dried product was brittle and results from IR analysis confirmed a sulfonated product. Since the handling properties of this sulfonated material were unsuitable for use in GSC, silica beads were selected as a support for Tenax-GC which then was sulfonated as described above in Experimental. This packing was white and had good handling properties for use in GSC. Results from titration of the H^+ form ion-exchange packing showed a capacity of 0.16 mequiv./g of packing or 7.4 mequiv./g of polymer for polymer loading of 2.2% (w/w). This value may be compared favorably to 5.4 mequiv./g of dry Dowex 1-XI¹⁸. Average carbon and hydrogen content by weight was 1.60% and 0.16% respectively. Copper content by weight was 0.35%.*

Comparisons of relative retention behavior for several aromatic and aromatic amine compounds on Cu^{2+} form ion-exchange column and OV-17/Chromosorb-W column are shown in Figs. 1 and 2. In Fig. 1 effects of temperature on retention of model compounds is shown in plots of k' vs. $1/T$ (°K). Plots show that aniline, N-methylaniline, and N,N-dimethylaniline are absorbed more strongly than similar aromatic carbon analogues which showed little or no retention on this column, even at temperatures as low as 90°C. Slopes of curves for aromatic amines show that values

* Silica beads following sulfonation had no H^+ capacity and showed no visible exchange with Cu^{2+} .

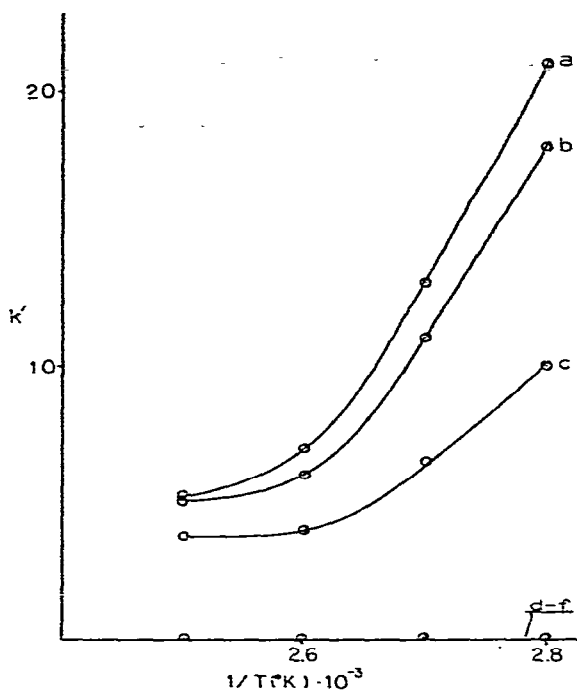


Fig. 1. Plot of k' vs. $(\text{temperature})^{-1}$ for 30 cm Cu^{2+} form ion-exchange column with compounds: (a) aniline, (b) *N*-methylaniline, (c) *N,N*-dimethylaniline, (d) ethylbenzene, (e) toluene, and (f) benzene. See Table I for values of V_g .

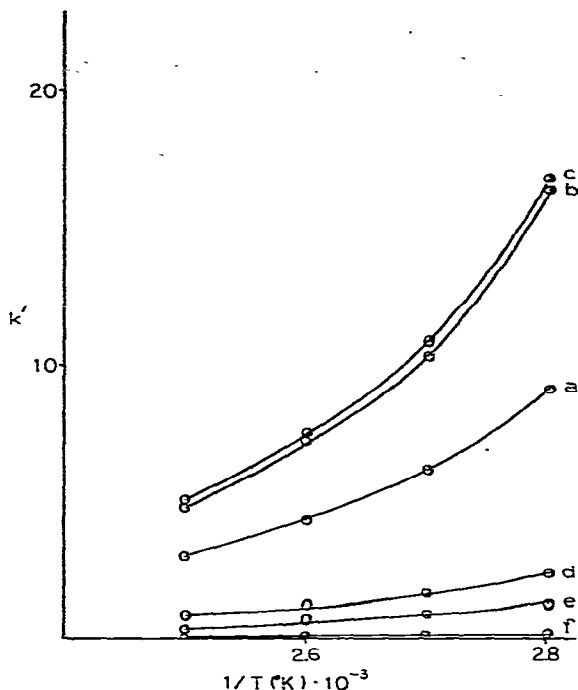


Fig. 2. Plot of k' vs. $(\text{temperature})^{-1}$ for 200 cm OV-17 on Chromosorb W column with same compounds as in Fig. 1. See Table I for values of V_g .

for V_g may be expected to be large at ambient temperature yet comparatively low at moderately elevated temperatures of 120 to 150°C. Such properties are necessary for successful application in thermal desorption analyses. Plots in Fig. 1 also show an elution order: *N,N*-dimethylaniline, *N*-methylaniline, and aniline as most strongly retained. Similar effects have been observed in solution in ligand-exchange chromatography¹⁹ and may result from steric hindrance in approach of R_3N : to Cu^{2+} in Lewis acid-base complexation²⁰. Retention behavior of these same compounds on a column of intermediate polarity is shown in Fig. 2. Again curves show aromatic amines are more strongly retained than aromatic carbon analogs. However, selectivity for amines was less since ethylbenzene and aniline showed values of α between only 3.3 to 3.9. Furthermore, elution order for the amines was completely reversed. Although values for k' appear similar for aromatic amines in Figs. 1 and 2, when estimated weight of liquid phases (0.016 g of Cu^{2+} form ion-exchange resin and 0.47 g of OV-17) are considered, values for distribution constant K , will differ substantially. Values for V_g for these compounds are given in Table I for both columns at temperatures of 120° and 90°C.

Typical of GSC, retention of amines on the Cu^{2+} form ion-exchange resin related to concentration in non-linear isotherms. Actual chromatograms are shown in Fig. 3 for aniline. By comparison to an analytical grade packed column, peak shape

TABLE I

SPECIFIC RETENTION VOLUMES FOR AROMATIC AND AROMATIC AMINE COMPOUNDS ON Cu^{2+} FORM IER AND OV-17 COLUMNS

Weight of packings were: OV-17, 1.587 g and IER, 0.545 g; surface area of Volaspher 0.9 m^2/g ; surface area of Chromosorb W 1.1 to 3 m^2/g .

	V_s			
	120°C		90°C	
	Cu^{2+} form ion-exchange resin (ml/g)	OV-17 (ml/g)	Cu^{2+} form ion-exchange resin (ml/g)	OV-17 (ml/g)
Benzene	0	0	0	1.3
Toluene	0	1.8	0	5.0
Ethylbenzene	0	3.5	4.8	11.8
Aniline	25.5	13.3	96.9	39.0
N-Methylaniline	24.4	21.4	83.3	69.9
N,N-Dimethylaniline	18.4	22.2	46.4	71.2

was poor with values for N (number of theoretical plates) of 28 and for H (height equivalent to a theoretical plate) of 1.4 cm with aniline at 100°C. These parameters clearly could be improved through increased attention to sieving the ion-exchange material before columns are packed and through optimization of carrier gas flow.

Partition coefficient, K , in gas-liquid chromatography with complexation interactions is shown in eqn. 1:

$$K = K^0 + K^0 K_1 C_s \quad (1)$$

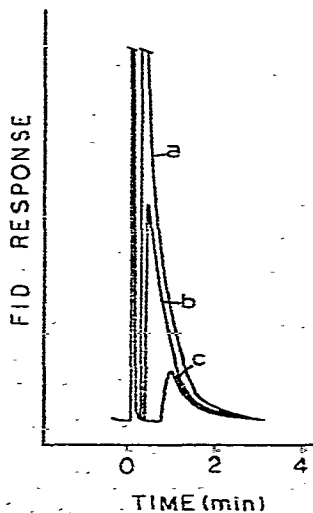


Fig. 3. Effect of mass on retention time for aniline on Cu^{2+} form ion-exchange column. Values are (a) 4.2 μg , (b) 2.1 μg , and (c) 0.7 μg .

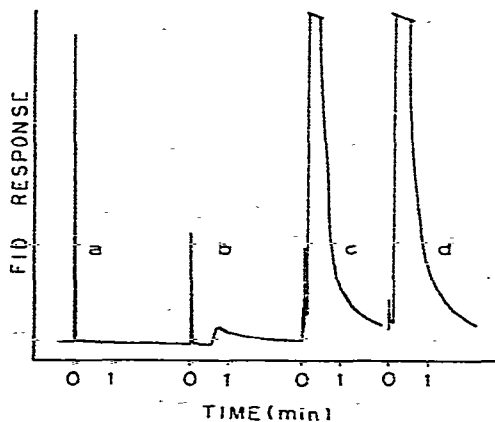


Fig. 4. Adsorption behavior of H^+ form ion-exchange resin for aromatic amines. Successive injections of (a) 2.5 μg of aniline and (b)-(d) 2.5 μg of N-methylaniline.

where K^0 is partition coefficient of solute with pure solvent, K_1 is the formation constant of the complex; and C_a is molar concentration of complexing agent in solution²¹. Although eqn. 1 has been modified for GSC²², extension to ion-exchange materials has not been made. Since interactions between the aromatic matrix and the aromatic amines may be expected to contribute to retention and since the ion-exchange packing may have been altered through sulfonation, the model closest to Cu^{2+} form ion-exchange column without specific interactions was first thought to be H^+ form ion-exchange resin. Representative results from a study of k' for aromatic amines using a H^+ form ion-exchange column are shown for *N*-methylaniline in Fig. 4. Results from four sequential replicate injections of pure compound with a trace of benzene impurity are presented as chromatograms which show complete adsorption of nearly 0.2 mg of aromatic amine. With subsequent injections, increasing amounts of compound were eluted successfully through the column. Uncoated silica beads were used as packing to determine if sites of adsorption on the support could adsorb amines and no adsorption was detected. While formation of an amine salt $\text{R}_3\text{N}^+\text{H}$ and adsorption is likely, the adsorptive capacity of the H^+ form ion-exchange resin could be restored by heating to 220°C. This process which was quantitatively reproducible was not investigated further and values for K^0 were not determined using H^+ form ion-exchange resin.

The Cu^{2+} form ion-exchange column was then reexamined for quantitative elution of aromatic amines. Adsorption of amines was noted for masses of 2 to 10 μg , roughly 10^3 less than for the H^+ form ion-exchange resin, but after several injections retention properties stabilized. These results are evidence that free $-\text{SO}_3\text{H}$ may be responsible for adsorption. After several injections of about 2 μg , percent elution was 100% vs. OV-17. This adsorptive behavior of the Cu^{2+} form ion-exchange resin also was restored after heating to 220°C, but no column bleed; evidence of decomposition of an amine salt, was detected.

Temperature stability of the Cu^{2+} form and H^+ form ion-exchange resins was tested first by heating from 75 to 220°C at 6°C/min. No shrinkage of the column bed volume was detected visually, but slight brown discoloration of the Cu^{2+} form resin was detected. However, retention behavior for aromatic amines did not change on the Cu^{2+} form resin column even after several hours at 220°C. The Cu^{2+} form resin was then kept at 250°C for 48 h. Results from study are shown in Table II as k' values for

TABLE II

VALUES OF k' FOR ANILINE AND *N*-METHYLANILINE VERSUS TIME FOR COLUMN TEMPERATURE OF 250°C

Measured at 100°C using 30 cm long column.

Time (h)	k' (aniline)	k' (<i>N</i> -methylaniline)
1	8.5	11.5
2	9.0	11.5
4	8.0	10.5
6	8.0	10.5
24	8.0	11.0
48	8.0	11.0

aniline and N,N-dimethylaniline. During this time, band broadening was increased slightly and k' values were decreased by only 5–6%.

CONCLUSIONS

Tenax-GC, a 2,6-diphenyl-*p*-phenylene oxide polymer may be successfully sulfonated using fuming sulfuric acid at 120°C. However, materials which are suitable for use in GSC are better prepared through the use of a solid support for the polymer which is then sulfonated. Results from elution behavior are consistent with complexation interactions of Cu^{2+} form ion-exchange resin with aromatic amines. This material is stable to at least 250°C with no column bed shrinkage. Furthermore, the material has properties and elution behavior which may be valuable for use in sorbent traps for selective adsorption of amines in complex environmental samples and in thermal desorption methods of such traps.

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REFERENCES

- 1 H. Prezler and R. Oehler, *Chem. Tech. (Leipzig)*, 15 (1963) 31.
- 2 G. M. Badger, N. Kowanko and W. H. F. Sasse, *J. Chromatogr.*, 13 (1964) 234.
- 3 A. G. Fogg and R. Wood, *J. Chromatogr.*, 20 (1965) 613.
- 4 M. A. Cawthorne, *J. Chromatogr.*, 25 (1966) 164.
- 5 B. T. Guran and L. B. Rogers, *Anal. Chem.*, 39 (1967) 632.
- 6 R. F. Hirsch, H. C. Stober, M. Kowblansky, F. N. Hubner and A. W. O'Connell, *Anal. Chem.*, 45 (1973) 2100.
- 7 R. Magidman, R. A. Bradford, D. H. Saunders and H. L. Rothbart, *Anal. Chem.*, 48 (1976) 44.
- 8 R. F. Hirsch and C. S. G. Phillips, *Anal. Chem.*, 49 (1977) 1549.
- 9 D. W. Emerson, R. R. Emerson, S. C. Joshi, E. M. Sorensen and J. E. Turek, *J. Org. Chem.*, 44 (1979) 4634.
- 10 R. van Wijk, *J. of Chrom. Sci.*, 8 (1970) 418.
- 11 K. Grob and G. Gröb, *J. Chromatogr.*, 62 (1971) 1.
- 12 A. Raymond and G. Guiochon, *Environ. Sci. Technol.*, 8 (1974) 143.
- 13 F. W. Karasek, D. W. Denny, K. W. Chan and R. E. Clement, *Anal. Chem.*, 50 (1978) 82.
- 14 S. H. Cadle, R. P. Mulawa, *Environ. Sci. Technol.*, 14 (1980) 718.
- 15 M. W. Dong, D. C. Locke and D. Hoffman, *Environ. Sci. Tech.*, 11 (1977) 612.
- 16 K. D. Brunneman, G. Stahnke and D. Hoffman, *Anal. Lett.*, All (1978) 545.
- 17 C. G. Horvath, B. A. Press and S. R. Lipsky, *Anal. Chem.*, 39 (1967) 1422.
- 18 J. X. Khym, *Analytical Ion-Exchange Procedures in Chemistry and Biology*, Prentice Hall, Englewood Cliffs, NJ, 1974, p. 64.
- 19 C. M. de Hernandez and H. W. Walton, *Anal. Chem.*, 44 (1972) 890.
- 20 L. A. du Plessis and A. H. Spong, *J. Chem. Soc.*, (1959) 2027.
- 21 E. Gil-Av and J. Herling, *J. Phys. Chem.*, 66 (1962) 1208.
- 22 D. F. Cadogan and D. T. Sawyter, *Anal. Chem.*, 43 (1971) 931.