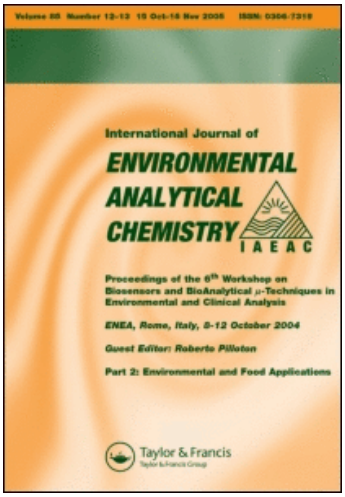

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Trace Amounts of Organic Pollutants in the Yellow River by Capillary Column Gas Chromatography-Mass Spectrometry

Wu Ren-ming[a]; Jiang Yi-man[a]; Ge Ning-chun[a]; Bai Shu-ming[a]; Qiao Shi-jun[a]
[a] Gansu Provincial Institute of Environmental Protection, The People's Republic of China

To cite this Article Ren-ming, Wu , Yi-man, Jiang , Ning-chun, Ge , Shu-ming, Bai and Shi-jun, Qiao(1985) 'Determination of Trace Amounts of Organic Pollutants in the Yellow River by Capillary Column Gas Chromatography-Mass Spectrometry', International Journal of Environmental Analytical Chemistry, 22: 1, 115 — 126
To link to this Article: DOI: 10.1080/03067318508076414
URL: http://dx.doi.org/10.1080/03067318508076414

Intern. J. Environ. Anal. Chem., 1985, Vol. 22, pp. 115–126
0306-7319/85/2202-0115 $18.50/0

Printed in Great Britain

Determination of Trace Amounts of Organic Pollutants in the Yellow River by Capillary Column Gas Chromatography-Mass Spectrometry†

WU REN-MING, JIANG YI-MAN, GE NING-CHUN, BAI SHU-MING and QIAO SHI-JUN

Gansu Provincial Institute of Environmental Protection, The People's Republic of China

(*Received November 25, 1984; in final form April, 12, 1985*)

The trace organic pollutants in the Yellow River enriched by a solvent extraction method were pre-separated into four different fractions of fatty hydrocarbons, polycyclic aromatic hydrocarbons, polar compounds and organic acids and were analyzed by the use of combined capillary column gas chromatography-mass spectrometry. Using the combined techniques of relative retention value, mass spectra and mass chromatogram, more than 60 organic pollutants were identified, among which 16 fatty hydrocarbons and 6 polycyclic aromatic hydrocarbons which were quantitatively analyzed. The concentration range of fatty hydrocarbon was 5–800 ng/l, and that of polycyclic aromatic hydrocarbon was 0–90 ng/l.

INTRODUCTION

Owing to the low content of organic pollutants in water, we usually use the method of solvent extraction, or the XAD resin adsorption and polyurethane plastic foam adsorption for effectively enriching the organic pollutants from large amounts of water before their

†Presented at the 14th Annual Symposium on the Analytical Chemistry of Pollutants, Barcelona, November 21–23, 1984.

GC/MS analysis. There are many papers or special publications describing those methods.[1-8] Coleman *et al.*[9] used counter permeation and solvent extraction to treat potable water in Cincinnati U.S.A., and identified 400 and more organic compounds by GC/MS analysis. Hites *et al.*[10] also used the solvent extraction method in the enrichment of organic pollutants in the river water of the Delaware, U.S.A., and analyzed nearly 100 organic compounds at the milli- or micro-gram per liter concentration by GC/MS. In our experiment, we have adopted the solvent extraction method and capillary column gas chromatography-mass spectrometry for the systematic analysis of low volatile organic pollutants in the water from the Yellow River.

EXPERIMENTAL

Instruments and reagents

The instruments used were the JGC-20 KFP gas chromatograph and the JMS-D100 mass spectrometer and JMA0231 data processing system.

Reagents Solvents: Hexane, benzene, methyl alcohol and acetone were redistilled in a whole glass distillation apparatus and collected for use. Each of the hexane and benzene fractions were taken respectively in 500 ml and concentrated to 50 microliters. They were injected into the gas chromatograph in 1 microliter and a blank test was made. No interference was found.

Silica gel: The silica gel used for the column chromatographic analysis was extracted in the extraction apparatus with redistilled chloroform for 48 hours. After drying, the gel was activated of 150°C for 4 hours and then stored in a drying apparatus. The silica gel volumn was purged with benzene. The benzene fraction was tested by chromatographically and no impurity was found. The activated aluminium oxide used for the column chromatographic analysis was activated at 400°C inside a muffle furnace.

Experimental collection

Sample collection Samples were collected from the surface water of the Yellow River located at 1.5 km downstream of the discharge site for the industrial waste water and domestic sewage from Lanzhou

city. A sample of 40 liters was collected on March 2, 1981 (normal water level period), 50 liters on August 10, 1981 and 56 liters on October 31, 1981 respectively. They were standing for 24 hr removing sand and the clear water was prepared for experimental use.

Extraction and preliminary separation of samples The sample was extracted with benzene and hexane and the extract was treated according to the operation process as shown in Figure 1. Consequently, four fractions of fatty hydrocarbon, polycyclic aromatic hydrocarbon, polar compound and organic acid were obtained and were determined respectively with GC/MS.

Experimental conditions for capillary column chromatograph The capillary column we used for the separation of fatty hydrocarbon and polycyclic aromatic hydrocarbons consisted of benzyl polysiloxane chemically bound on the silica gel (provided by the Lanzhou Institute of Chemico-physics, Academy of Sciences), column length 18 m, I.D. 0.3 mm. Helium was used as carrier gas with a pressure of 0.8 kg/cm^2. The temperature at the inlet was 310°C. The initial temperature of the column box was 120°C, it lasted for 2 minutes and then was warmed up to 300°C with a programmed temperature increase of 5°C per minute and maintained until the appearance of the last sample peak. The organic acid and the polar compound fractions were separated by another PEG-20M stainless steel capillary column (length 45 m, I.D. 0.25 mm), with the pressure of helium being 1.35 kg/cm^2; inlet temperature 250°C; initial box temperature 120°C for 3 minutes and then warmed up to 220°C with a programmed temperature of 4°C per minute. The splitless technique was adopted for the injection of samples.[11,12]

Experimental conditions for mass spectrometry The connection between the capillary column and the mass spectrometer ions source was according to Henneberg; resolution power of mass spectrum, 1,000; accelerating voltage, 3,000 V; ionogenic voltage 75 V; ionogenic current, 300 μA, temperature of ionic source, 230°C and temperature of interface 250°C.

The scanning range and the scanning time interval of the spectrum were respectively: for the polycyclic aromatic hydrocarbon fraction, m/e 50–350, $T = 8$ sec; for the fatty hydrocarbon and the organic acid fraction, m/e 28–600, $T = 10$ sec.

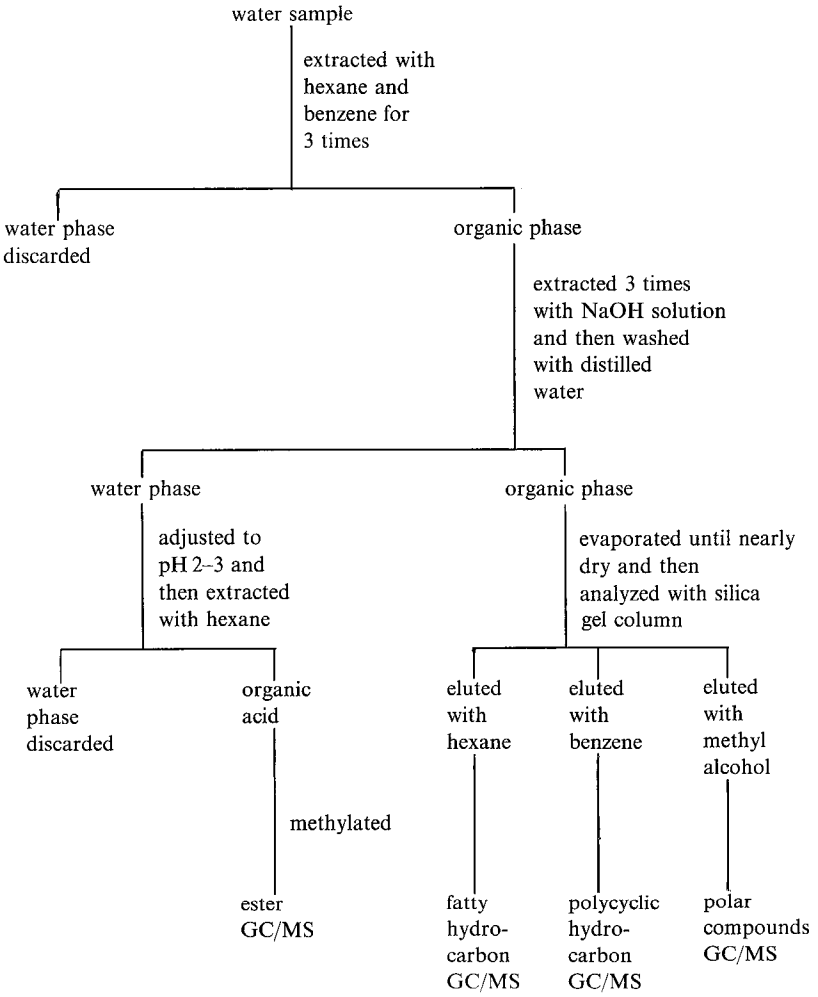

FIGURE 1 Pre-separation of sample.

RESULTS AND DISCUSSIONS

Because of the complex composition of the organic matter in water, the extraction liquid must be pre-separated before doing the GC/MS analysis. In this way some fractions of different properties may be separated into different classes of compounds. There are several

methods for the pre-separation. We used a classification of the extracted matters into acidic, basic, and neutral components. The latter was further separated into fatty hydrocarbons, polycyclic aromatic hydrocarbons and polar compounds through a chromatographic column (I.D. 1 cm, packed with a 0.5 cm layer of active aluminium oxide and 11.5 cm of active silica gel). It was shown that our pre-separation method gave satisfactory results and no interference was found between each of the fractions.

Our extraction efficiency was also tested and verified. We chose three different polycyclic aromatic hydrocarbons, three different fatty hydrocarbons, two different organic acids and one phthalic ester and took them as the standard samples. They were made up in one liter of distilled water to coincide with the concentration (ng/l) of the real sample. We then found a mean recovery ratio of 88% (see Table I).

TABLE I

Recovery ratios of standard samples.

Compounds	Recovery ratio (%)				Average of recovery ratio (%)
	1	2	3	4	
Phenanthrene	75	85	74	61	74
Chrysene	89	92	96	95	94
Perylene	94	85	85	94	90
N-eicosane	88	90	93	96	93
N-tetracosane	92	92	93	91	92
N-octacosane	95	92	95	93	94
Lauric acid	80	94	79	92	84
Non-decanoic	72	79	72	70	73
Diethyl phthalate	86	85	95	70	84

Qualitative results

Four different fractions were analyzed by gas chromatography and mass spectrometry and 60 different compounds were determined, which included 34 different alkane hydrocarbons and alkene hydrocarbons, 21 different polycyclic aromatic hydrocarbons, 3 different acids and 6 different esters.

Fatty hydrocarbon The fatty hydrocarbon fraction collected after elution was analyzed from a chromatogram as shown in Figure 2. The relative retention time of the peaks Nos. 2, 9, 16 and 24 were totally coincident with the relative retention time of the standard samples of N-17 alkane, N-20 alkane, N-24 alkane and N-28 alkane. For more conclusive evidence, we also made the chromatogram of the total ion current of fatty hydrocarbons and also the mass chromatogram of m/e 85 fragmentary ions and the molecule–ion peaks (see Figure 3). It was seen that each of the peaks there was a m/e 85 characteristic fragmentary ion, and at an interval of each 14 mass units there appeared a molecule–ion peak of hydrocarbon. Those peaks were arranged in good order from C_{16} alkane to C_{35} alkane. Besides, there was a mass spectrogram of different alkane hydrocarbons corresponding to each of the peaks (being coincident with the standard mass spectrogram of same alkane hydrocarbons). Thus we obtained the fatty alkane hydrocarbons from C_{16} to C_{35} alkanes and the C_{15} alkene up to C_{35} alkene (see Table II).

Polycyclic aromatic hydrocarbons The pollution effect caused by the carcinogenic polycyclic aromatic hydrocarbons in water has attracted great attention by the public, and the WHO has definitely specified the upper six polycyclic aromatic hydrocarbons at 250 millimicro grams per liter.[16] Therefore the determination of the composition and contents of the polycyclic aromatic hydrocarbons in water is of great importance. The determination with a mass spectrograph is convenient and the molecule–ion peaks in the mass spectra are easily identified. However, owing to the different

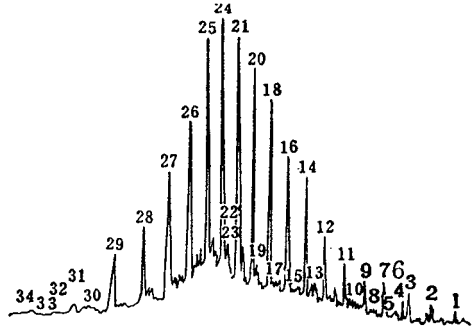

FIGURE 2 Chromatogram of fatty hydrocarbons. For peak identity see Table II.

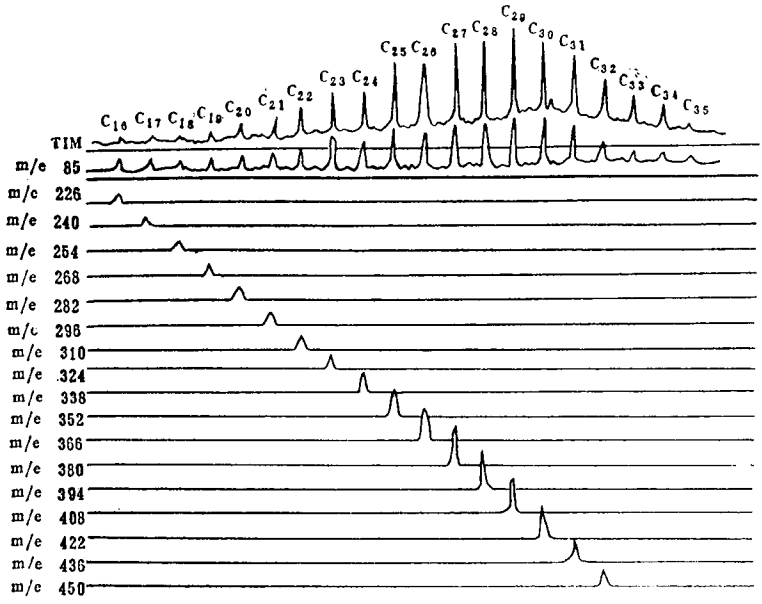

FIGURE 3 Mass chromatogram. For peak identity see Table II.

positions of substituents, a large number of isomers can occur. In our experiment, we used the chemical bond type of capillary column to find separate those isomers and then we obtained satisfactory results.[12] The number of isomers was then determined by the further use of mass chromatography. Figure 4 showed the chromatogram of

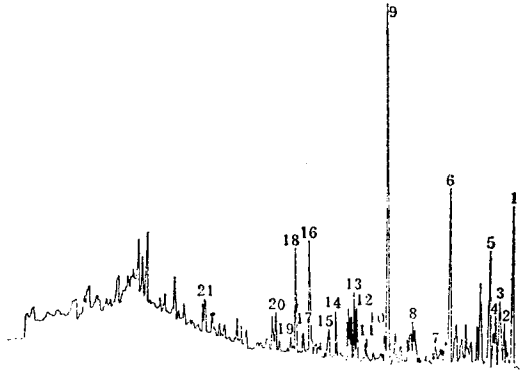

FIGURE 4 Chromatogram of PAHs. For peak identity see Table III.

TABLE II

Fatty hydrocarbons in the Yellow River water.

Peak no.	Compounds	M.W.	Standard sample relative retention time	Sample relative retention time	Methods of identification
1	Hexadecane	226	—	—	MS
2	Heptadecane	240	0.582	0.580	ST-MS
3	Octadecane	254	—	—	MS
4	Isotetradecane	198	—	—	MS
5	Heptadecane	238	—	—	MS
6	Pentadecene	210	—	—	MS
7	Non-adecane	264	—	—	MS
8	Octadecene	252	—	—	MS
9	Eicosane	282	0.959	0.955	ST-MS
10	Heptadecene	238	—	—	MS
11	Heneicosane	296	—	—	MS
12	Docosane	310	—	—	MS
13	Eicosene	280	—	—	MS
14	Tricosane	324	—	—	MS
15	Heneicosene	294	—	—	MS
16	Tetracosane	338	1.000	1.000	ST-MS
17	Tricosene	322	—	—	MS
18	Pentacosane	352	—	—	MS
19	Tricosene	322	—	—	MS
20	Hexacosane	366	—	—	MS
21	Heptacosane	380	—	—	MS
22	Eicosene	280	—	—	MS
23	Hexacosene	364	—	—	MS
24	Octacosane	394	1.189	1.192	ST-MS
25	Non-acosane	408	—	—	MS
26	Triacontane	422	—	—	MS
27	Hentriacontane	436	—	—	MS
28	Dotriacontane	450	—	—	MS
29	Tritriacontane	464	—	—	MS
30	Hentriacontene	434	—	—	MS
31	Dotriacontene	448	—	—	MS
32	Tetratriacontane	478	—	—	MS
33	Tritriacontene	462	—	—	MS
34	Pentatriacontane	492	—	—	MS

polycyclic aromatic hydrocarbon fractions. Among the water samples collected in the period of normal water level, 21 polycyclic aromatic hydrocarbons were identified (see Table III), with samples collected during the flood period, nitrogenous polycyclic aromatic hydrocarbons such as the 2,4-diphenylazaprrole were observed.

Organic acids and polar components Since there are no molecule–ion peaks and other characteristic peaks in the mass spectrogram of fatty acids, the acid should be methylated so that the molecule–ion

TABLE III

PHA's in the Yellow River water.

Peak no.	Compounds	M.W.	Standard sample relative retention time	Sample relative retention time	Methods of identification
1	Biphenyl	154	0.411	0.415	ST-MS
2	Dimethyl-naphthalene	156	—	—	MS
3	Dimethyl naphthalene	156	—	—	MS
4	Acenaphthylene	152	—	—	MS
5	Acenaphthene	154	0.505	0.503	ST-MS
6	Fluorene	166	0.603	0.607	ST-MS
7	Methyl fluorene	180	—	—	MS
8	Dimethyl fluorene	194	—	—	MS
9	Phenanthrene	178	0.781	0.783	ST-MS
10	Anthracene	178	0.789	0.793	ST-MS
11	Methyl-4H-cyclo-pentanophenanthrene	204	—	—	MS
12	Methyl phenanthrene	192	—	—	MS
13	Methyl phenanthrene	192	—	—	MS
14	Ethyl phenanthrene	206	—	—	MS
15	Ethyl phenanthrene	206	—	—	MS
16	Fluoranthene	202	1.000	1.000	ST-MS
17	Benzacenaphthylene	202	—	—	MS
18	Pyrene	202	1.039	1.038	ST-MS
19	Methyl fluoranthene	216	—	—	MS
20	Benzo(b)fluorene	216	1.119	1.120	ST-MS
21	Benzo(a)anthracene	228	1.269	1.265	ST-MS

peaks and the characteristic peaks for m/e 74 ions might occur. For this reason, we used trifluoro-boron as the catalyst added in dried methanol to transform the fatty acid into an ester. Components such as myristic acid, palmitic acid and arachidic acid were determined in this way. Figure 5 shows a chromatogram of polar compounds in water.

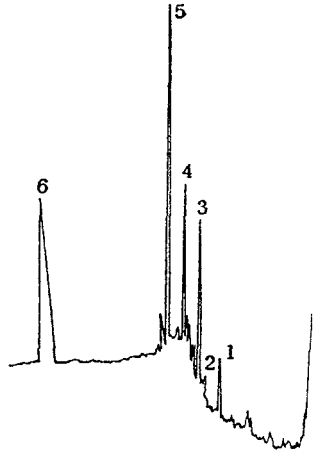

FIGURE 5 Chromatogram of polar organic compounds.

Quantitative results

In our quantitative determination of 6 polycyclic aromatic hydrocarbons and 18 fatty hydrocarbons, we used phenanthrene and chrysene representing respectively the tricyclic and the tetracyclic systems in polycyclic aromatic hydrocarbons and made up a standard solution of 100 μg/ml. Sample contents were calculated from the standard curve made according to the peak area of the chromatogram. The quantification contents of N-16 alkane up to N-30 alkane were calculated from the standard curve made with N-24 alkane.

In order to understand fully the variation of concentration of the organic matters in the Yellow River in different seasons, we collected the water samples at the same spot on March, August and October 1981, and made a comparison between their contents. The numerical data in Table IV indicated that the content of each of the fatty

TABLE IV
Contents of PAH and fatty hydrocarbons in the Yellow River water (ng/l) in 1981.

Compound	March	August	October
Phenanthrene	93.1	8.0	56.1
Anthracene	7.7	0.8	9.5
Fluoranthene	25.0	10.0	22.7
Pyrene	24.5	8.8	19.6
Benzo(b)fluorene	10.6	4.0	18.5
Benzo(a)anthracene	9.6	0	7.3
Hexadecane	18.4	4.8	317
Heptadecane	25.3	10.8	766
Octadecane	32.2	19.2	356
Non-adecane	41.4	31.2	462
Eicosane	27.6	46.6	369.
Heneicosane	36.8	45.6	229
Docosane	57.5	40.8	160
Tricosane	138	41.4	127
Tetracosane	175	36.0	112
Pentacosane	278	54.6	140
Hexacosane	322	60.0	141
Heptacosane	320	72.0	180
Octocosane	223	69.6	153
Non-acosane	255	114	207
Triacontane	243	95.5	120
Hentriacontane	184	110	116
Dotriacontane	138	58.2	51.7
Tritriacontane	94.3	45.6	49.5

hydrocarbons in the Yellow River water reached tens or several hundreds of millimicrogram/liter. The total content of all fatty hydrocarbons amounted to 2,610 ng/l in March, 952 ng/l in August and 4,055 ng/l in October. The August content was the lowest, the March content was 2.7 times that of August and the October content was 4.3 times higher than is August. As for the polycyclic aromatic hydrocarbons, the content of each of the PAH's ranged from zero up to about 90 ng/l. The total content of the six PAH amounted to 170 ng/l in March, 31.6 ng/l in August and 134 ng/l in October. The content in August was again the lowest, the March content was 5.4 times that of August and the October content was 4.2 times that of August. If we make a rough estimation for the total

content of polycyclic aromatic hydrocarbons by the use of their total chromatogram, it can be found that the lower content was in August, being 385 ng/l, and the highest content in March, being 1,400 ng/l. Comparing these values (as shown in Table IV) with those total contents of polycyclic aromatic hydrocarbons in rivers of other countries, we can observe that the values obtained from the Yellow River are on an intermediate level compared to the range of values determined by some foreign countries.

References

1. W. L. Budde and J. W. Eichelberger, *Organics Analysis Using GC/MS* (Ann Arbor Science, 1979), pp. 41–74.
2. J. Albaiges, *Analytical Techniques in Environmental Chemistry* (Pergamon Press, 1978).
3. L. H. Keith, *Identification and Analysis of Organics Pollutants in Water* (Ann Abor Science, 1976).
4. R. Shinohara, *Water Research* **15,** 535 (1981).
5. F. M. Benoit, *Intern. J. Environ. Anal. Chem.* **6,** 277 (1979).
6. C. Shu-ying, *Collective J. Environ. Sci., China* **6–7,** 128 (1981).
7. D. Shi-gui, *Proceedings of Second Environmental Science Symposium of the University of Beijing, China,* pp. 145–154 (1981).
8. Z. Y. Ying, *Environ. Protective Sci.* **4,** 40 (1981).
9. W. E. Coleman, *Environ. Sci. Technol.* **14,** 576 (1980).
10. D. Shuetzle, Monitoring toxic substances, *ACS Symposium Series* **94,** 63 (1979).
11. F. J. Yang, *J. Chromatogr.* **158,** 91 (1978).
12. W. Ren-ming, *Mass Spectr.* **I,** 3 (1981).
13. *Analytical Instruments, Japan* **12(I),** 9 (1980).
14. F. W. McLafferty, *Registry of Mass Spctral Data* (John Wiley and Sons, 1974).
15. *Peak Index of Mass Spectra* (Mass Spectrometry Data Centre, 1974).
16. *International Standard for Drinking Water, 3rd ed.* (World Health Organization Geneva, Switzerland, 1971).
17. M. L. Lee, *Anal. Chem.* **48,** 410 (1976).