

# Ion Chromatographic Analysis of Water-Soluble Anions in the Atmosphere in Amman, Jordan

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In the summer of 1995, samples of airborne particles were collected in the Amman area of Jordan. Ion chromatography (IC) was used for the determination of anions in these samples. Four anions were identified and quantified in the atmosphere of Amman. The concentration ranges of  $F^-$ ,  $Cl^-$ ,  $NO_3^-$  and  $SO_4^{2-}$  were 0.04 - 3.3, 2.25 - 15.7, 1.96 - 8.39 and 16.88 - 41.33  $\mu g/m^3$ , respectively. The study shows that  $Cl^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$  are the major anions of air particulate, and the concentration of  $SO_4^{2-}$  exceeds that of some other cities worldwide. The total suspended particles (TSP) value was determined to be 66 to 326  $\mu g/m^3$ .

## Introduction

One of the principle advantages of Ion chromatography is the simultaneous determination of a mixture of ions with minimum sample treatment in a relatively short time. Additionally, IC provides high sensitivity and very low detection limits. For these reasons, IC has been used for many environmental applications since its introduction by Small et al.<sup>1</sup>. Anions as well as cations in air particulates were determined by IC with higher accuracy and precision than conventional wet chemical methods<sup>2</sup>. The determination of sulfate and nitrate in air particulates is especially important because of their relevance to the problems of air pollution and acid rain<sup>3-5</sup>. Fluoride is considered to be detrimental to vegetation and animals<sup>6</sup>.

Amman, the capital of Jordan, at the end of 1994 had a population exceeding 1.5 million with approximately 200,000 automobiles. Generally, there is a lack in regulations for controlling and monitoring automobile emissions in Jordan. Additionally, the crude oil used in Jordan is of relatively high sulfur content, ranging between 2 and 8 %. Since there is no published data on the levels of atmospheric pollutants in Jordan, the purpose of this study is to present the analysis of inorganic anions in the air particulates of Amman's air. Other pollutants in Amman's atmosphere are under investigation in our laboratory, and the results will be published upon completion.

## Experimental

### Reagent

All chemicals were of analytical reagent grade, and all reagents and mobile phase and standard solutions were prepared using HPLC-water from Lab Scan, USA. The standard mixture containing  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ , and  $SO_4^{2-}$  ions was purchased from the Dionex corporation.

### Instrumentation and materials

The sampling pump, (Stuplex Air Sampler Division, Brooklyn, NY, USA), was operated at a flow rate of 25l/min for a ten-hour sampling period. The sample analysis was carried out on a Dionex DX-100 Ion Chromatograph with conductivity detector (30  $\mu s$  FS), from Dionex, Sunnyvale, CA, USA. Anions were separated on an AS4A SC ion exchange column (25 cm  $\times$  4 mm I.D) with an AG4A-SC ground column 4 mm I.D, and detected after suppression with an ASR1 anion self-regenerating suppresser. The injection volume was 25  $\mu L$ , and the flow rate was 2.0 ml/min. The chromatograms were recorded on a 4400 integrator from Dionex.

### Samples and Treatment

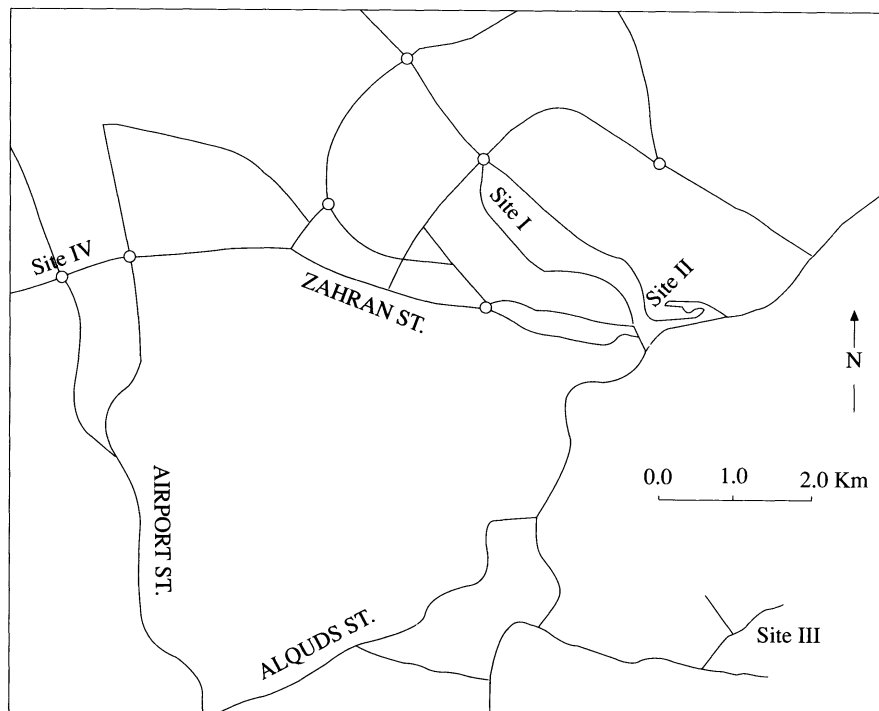
Samples of air particulates were collected during the daytime in August 1995 (Summer season) from four sites in the Amman area representing different traffic conditions: site I: Abdally, where a large traffic station with diesel-powered buses is located on major highway; site II: downtown area; site III; Sahab, south of Amman, where light industrial companies are located; site IV: 8th circle, which is a region of medium and steady traffic. The locations of the sampling sites are shown in Figure 1. From each site, samples were collected in a glass fiber filter with a 0.45  $\mu m$  pore size and a diameter of 45 mm from Gelman Science, Ann Arbor, MI, USA, on a ten-hour basis for the entire month of August, 1995. All filter papers were weighed before and after sampling to determine the weight of air particulates. The sample filters were kept refrigerated in closed bottles until one to two hours prior to IC analysis. Extraction was carried out by heating the sample in a water bath for thirty minutes at 50°C and then by sonication for 20 minutes with 15 ml of mobile phase, which consists of 1.8 mM  $Na_2CO_3$  and 1.7 mM  $NaHCO_3$  in HPLC water<sup>7,8</sup>. After filtration the volume was adjusted to 25 ml with the mobile phase in polyethylene volumetric flasks. The blank was prepared by extracting five glass fiber filters as was done with the sample. This eluent was chosen for its availability, suitability with suppressed IC mode, and separation of the sample components in a short time. Other investigators used different mobile phases, such as gluconic acid-boric acid aqueous solution in a nonsuppressed IC mode<sup>19</sup>. They were able to obtain a satisfactory separation of the anions of interest within 18 minutes.

Wind speed data during the sampling period was collected from two sites, at Amman Airport, east Amman, and at Sweileh, west Amman. The wind was mostly quiet, seldom reaching an average of 14 knots, and lasted only for a few hours<sup>9</sup>.

## Results and Discussion

Ion chromatography is an outstanding technique in the analysis of ions. Calibration was undertaken with mixed  $F^-$ ,  $Cl^-$ ,  $NO_3^-$  and  $SO_4^{2-}$  ions. Good linearity was obtained between the peak area and concentration

over the range 0.1-6.67 ppm, 0.15-15 ppm, 0.5-15 ppm and 0.75-40 ppm for  $F^-$ ,  $Cl^-$ ,  $NO_3^-$  and  $SO_4^{2-}$ , respectively (Figure 2). The correlation coefficients ( $r$ ) were 0.9991, 0.9992, 0.9988 and 0.9992 for  $F^-$ ,  $Cl^-$ ,  $NO_3^-$  and  $SO_4^{2-}$ , respectively.

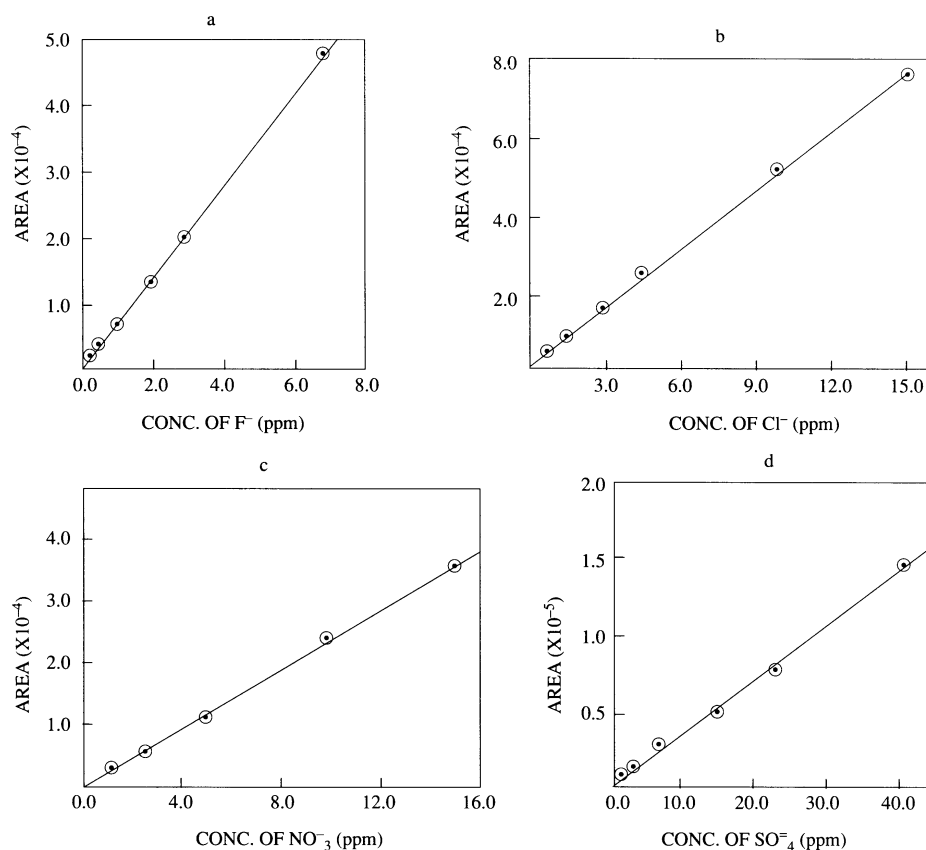


**Figure 1.** Location of sampling sites. Site I: Abdali, Site II: Downtown, Site III: Sahab, and Site IV: 8th Circle.

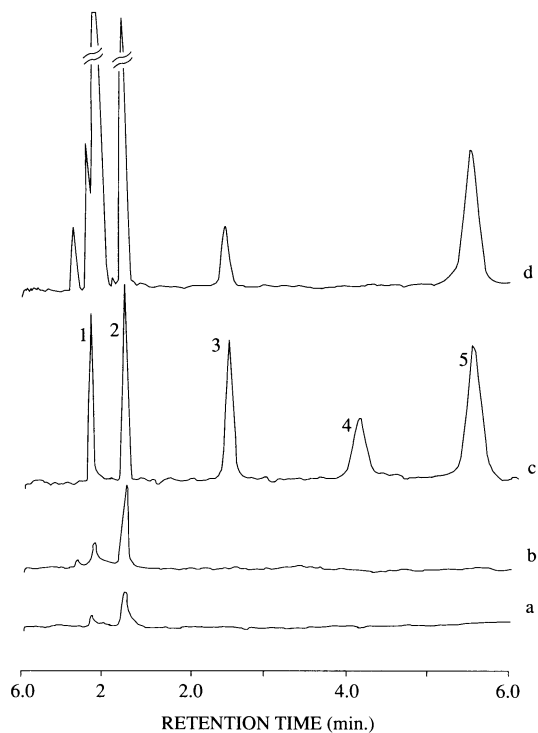
The blank was prepared by extracting five filter papers with the extracting solvent and analyzed similarly to the samples. It showed some chloride background, which might have been preadsorbed on the glass fiber filter papers. The area of this background was subtracted from the chloride peak in each sample.

Typical chromatograms of the mobile phase, a blank, a standard mixture and an air particulate sample are shown in Figure 3. The chromatogram of the air particulate sample illustrates a satisfactory separation of the analytes of interest within less than 6 minutes. In addition, all particulate samples contain fluoride, chloride, nitrate and sulfate as major components. The figure shows that fluoride peak overlaps with unidentified peak, which is labeled as water soluble organics (WSO)<sup>19</sup>. This overlap may create inaccurate determination of fluoride ions.

The average monthly concentrations ( $\mu g/m^3$ ) of fluoride, chloride, nitrate and sulfate in the air particulate samples from the four sampling sites are summarized in Table 1, in which it may be seen that the average aerosol chloride and sulfate concentrations frequently exceed those of fluoride and nitrate in all sampling locations. In addition, the mean sulfate concentration exceeds that of chloride in all locations. Table 1 also shows higher average concentrations of sulfate and nitrate in site II than in other areas, which could be due to higher traffic rates at this site, and the type of fuel used in Jordan. The normal nitrate range in the atmosphere is  $0.1-10 \mu g/m^3$ <sup>10</sup>, and Table 1 shows that the results are all within the normal range. Sites I and IV show relatively high levels of fluoride, which may be due to the closeness of these sites to a major source of fluoride containing dust, the phosphate industry<sup>11</sup>. The total suspended particulates figure at site I largely exceeds those of other sites, perhaps because of the type of motor vehicles using this site, mainly diesel-powered buses and trucks.



**Figure 2.** Calibration curves for F<sup>-</sup>, a; Cl<sup>-</sup>, b; NO<sub>3</sub><sup>-</sup>, c; and SO<sub>4</sub><sup>=</sup>, d.

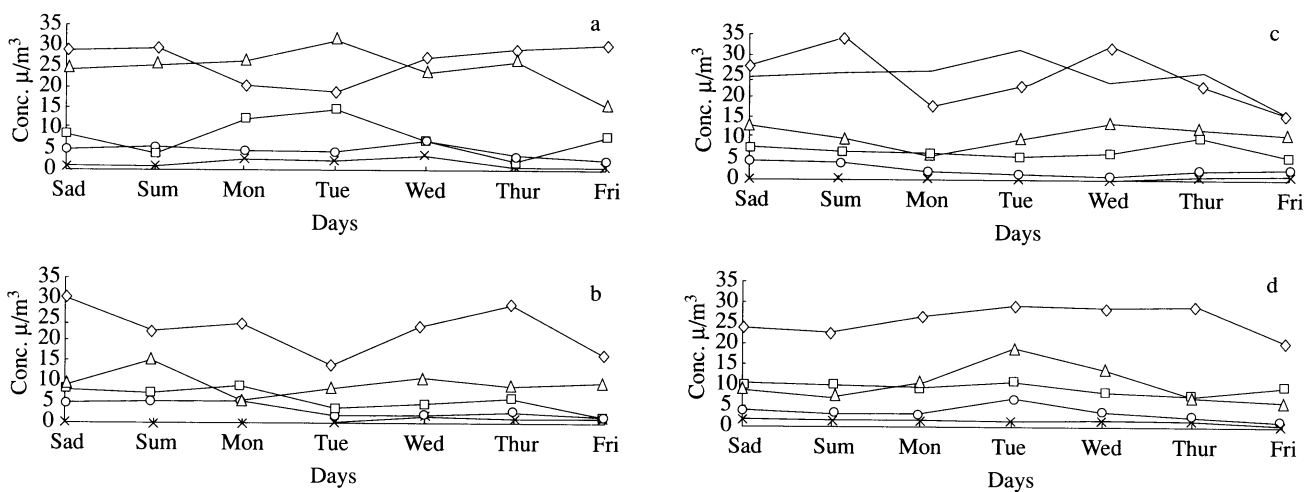


**Figure 3.** Chromatograms of the mobile phase (a), a blank (b), a standard mixture (c), and air particulate sample extract (d). Column, AS4A-SC (25 cm × 4mm I.D) eluent, 1.8 mM Na<sub>2</sub>CO<sub>3</sub> and 1.7 mM NaHCO<sub>3</sub>; flow rate, 2.0 mL/min; detection, suppressed conductivity; sample, 25 μL; peaks: 1 = F<sup>-</sup>, 2 ppm; 2 = Cl<sup>-</sup>, 3 ppm; 3 = NO<sub>3</sub><sup>-</sup>, 10 ppm; 4 = SO<sub>4</sub><sup>=</sup>, 15 ppm.

**Table 1.** Ambient Concentrations ( $\mu\text{g}/\text{m}^3$ ) of Anions and TSP in Air Particulate Samples at Amman City, Jordan (August 1995).

Site	Species	Average	CV%	Minimum	Maximum
I	$\text{F}^-$	1.72	49.6	0.77	3.30
	$\text{Cl}^-$	8.58	53.7	2.49	15.70
	$\text{NO}_2^-$	4.87	26.3	3.36	7.22
	$\text{SO}_4^-$	26.80	17.5	19.6	31.40
	TSP	257.00	17.9	173.00	326.00
II	$\text{F}^-$	0.38	79.8	0.04	0.90
	$\text{Cl}^-$	7.71	43.5	2.25	12.50
	$\text{NO}_3^-$	4.89	45.7	2.43	8.39
	$\text{SO}_4^-$	31.90	25.1	19.67	41.33
	TSP	142.10	30.0	79.00	213.00
III	$\text{F}^-$	0.66	107.6	0.05	1.93
	$\text{Cl}^-$	8.03	22.4	6.68	12.01
	$\text{NO}_3^-$	3.10	34.5	1.96	4.59
	$\text{SO}_4^-$	25.50	27.0	16.88	34.48
	TSP	120.70	23.8	66.0	153.00
IV	$\text{F}^-$	1.49	21.4	1.18	1.96
	$\text{Cl}^-$	10.16	12.5	8.56	11.69
	$\text{NO}_3^-$	3.99	48.9	2.74	7.44
	$\text{SO}_4^-$	26.40	15.0	21.90	30.57
	TSP	111.20	46.7	73.00	200.00

Figure 4 illustrates the average daily variation of anions in airborne particles and TSP during the month of August, 1995, measured at the four sites (I-IV). Generally, fluoride and nitrate show a steady time profile all locations. Chloride time profiles show almost steady levels, except at site I, where higher levels of  $\text{Cl}^-$  show up on Mondays and Tuesdays. On the other hand, sulfates and TSP show significant variation during the week, except at site IV, perhaps because of the normal steady traffic at this site.


**Figure 4.** Average daily variations of  $\text{F}^-$  ( $\times$ ),  $\text{Cl}^-$  ( $\square$ ),  $\text{NO}_3^-$  ( $\circ$ ), and  $\text{SO}_4^-$  ( $\diamond$ ) in air particulates and TSP  $\times 10^{-1}$  ( $\Delta$ ) taken from Site I, a; Site II, b; Site III, c; and Site IV, d.

A comparison of the average concentrations of anions in air particulates and TSP is presented in Table 2, which reveals that fluoride and nitrate levels in Amman's air particulates are intermediate with respect to those of other cities worldwide. On the other hand, chloride and sulfate levels in Amman are much higher than those of other places. This may be attributed to the type of motor vehicle fuel used in Jordan, mostly leaded and sulfur rich. It is clear from Table 2 that the limits of  $75 \mu\text{g}/\text{m}^3$  as the annual average set by US Environmental Protection Agency was exceeded by almost double during the sampling period.

**Table 2.** Comparison of Anions and TSP Levels in Airborne Particulates in Amman and Other Cities ( $\mu\text{g}/\text{m}^3$ ).

City (sampling period)	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>=</sup>	TSP
This work*					
Amman/Jordan (August 95)	1.06 ± 0.64	8.62 ± 1.10	4.21 ± 0.85	27.65 ± 2.88	157.8 ± 67.4
Other work					
Delhi / India <sup>12</sup> (N/A)					700
London/England <sup>12</sup> (N/A)					150
Smoky Mountain/USA <sup>13</sup> (N/A)		0.017	0.30	12.0	29.6
Houston/USA <sup>14</sup> (N/A)		0.35	2.05	17.8	69.0
San Jose/USA <sup>15</sup> (N/A)			5.49	2.27	
River side/USA <sup>15</sup> (N/A)			21.78	8.43	
Los Angeles/USA <sup>15</sup> (N/A)			15.81	14.8	
Gotenberg/Sweden <sup>16</sup> (Sept 77)			0.06-3.1		
Beigin/China <sup>5</sup> (Autamn 85)			21.7	25.1	
Cincinnati/USA <sup>6</sup> (N/A)	0.68				
Downey/USA <sup>2</sup> (N/A)	3.99-6.01	1.67-3.27	1.19-15.17	1.0-22.6	
Telluride/USA <sup>11</sup> (winter/86)					155-214
Leeds/UK <sup>17</sup> (N/A)		0.78	1.91	2.95	
Different cities/Chile <sup>18</sup> (Different periods)		0.04-5.35			104-315
Halle/Germany <sup>19</sup> (June, July 92)		0.3	2.7	9.4	66

N/A not available

\*The values are expressed in terms of average ± CV%.

## Reproducibility

Repeated analyses of a single particulate filter sample gave relative standard deviations (%RSD) of 9.8%, 5.9%, 4.66% and 2.55% for anions  $F^-$ ,  $Cl^-$ ,  $NO_3^-$  and  $SO_4^{2-}$ , respectively, while the total area gave 2.6%. These results show that the precision of the peak areas of the anions is acceptable despite the relative height of the %RSD of  $F^-$ , which is due to the overlap of the fluoride peak with the unidentified peak (WSO) following it (Figure 3d).

## Conclusions

The results presented in this work illustrate that ion chromatography is convenient for the simultaneous determination of fluoride, chloride, nitrate and sulfate in air particulate samples in less than 6 minutes with adequate precision and sensitivity. However, utilizing the carbonate - bicarbonate eluent is less convenient for fluoride determination, due to the overlap of  $F^-$  peak with the unidentified peak.

The dominant inorganic anions in the air particulate of Amman's atmosphere are  $Cl^-$ ,  $NO_3^-$  and  $SO_4^{2-}$ , with sulfate as the major component. The high levels of sulfates might be due to the relatively high sulfur content of the automotive fuels used in Jordan. Finally, the total suspended particulate level exceeds the recommended value set by the USEPA.

## Acknowledgement

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## References

1. H. Small, T. Stevens and W.C. Bauman, **Anal. Chem.**, **47**, 1801 (1975).
2. J. Lathouse and W.R. Coutant in "Ion Chromatographic Analysis of Environmental Pollutants", E. Sawicki, J.D. Mulik and E. Wittgenstien Eds.), Ann Arbor Science: Ann Arbor, Mich. 53 (1978).
3. W.M. Lewis and M.C. Grant, **Science**, **207**, 176 (1980).
4. M. Achilli, L. Romele, W. Martinotti and G. Sommariva, **J. Chromatogr.**, **706**, 241 (1995).
5. S. Mou, **J. Chromatogr.**, **546**, 325 (1991).
6. L.A. Elfers and C.E. Decker, **Anal. Chem.**, **40**, 1658 (1968).
7. P.K. Mueller, B.V. Mendoza, J.C. Collins and E.S. Wilgus in "Ion Chromatographic Analysis of Environmental Pollutants", E. Sawicki, J.D. Mulik and E. Wittgenstien Eds.), Ann Arbor Science: Ann Arbor, Mich., 77 (1978).
8. Dionex Application Note AN 2R, August 1991.
9. Meteorology Department Report, August 1995: Amman - Jordan.
10. J.P. Londge JR. (Ed.), "Methods of Air Sampling and Analysis" 3rd Ed., Lewis Publishers, Inc. USA, 382 (1989).
11. A.L. Dresser, **JAPCA**, **38**, 1419 (1988).
12. S.M. Khopfar, "Environmental Pollution Analysis", Wiley Estern Ltd.: New Delhi, 2 (1993).

13. T.G. Dzubay, R.K. Stevens, C.W. Lewis, D.H. Hern, W.J. Courtney, J.W. Tesch and M.R. Mason, **Environ. Sci. Technol.**, **16**, 514 (1982).
14. R.K. Stevens, T.G. Dzubay, C.W. Lewis and R.W. Shaw, **Jr.**, **Atmos. Environ.**, **18**, 261 (1984).
15. B.R. Appel, Y. Tokiwa, T. Hsu, E.L. Kothny and E. Hahn, **Atmos. Environ.**, **19**, 1525 (1985).
16. P. Grennfelt, **Atmos. Environ.**, **14**, 311 (1980).
17. M.J. Willison and A.G. Clarke, **Anal. Chem.**, **56**, 1037 (1984).
18. C.M. Romo-Kroger, **Environ. Pollut.**, **68**, 161 (1990).
19. H. Schumann and M. Ernst, **J. Chromatogr.**, **640**, 241 (1994).