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Microscale detection of polychlorinated biphenyls using two-step laser mass spectrometry

Tania B. Mahajan[a], Upal Ghosh[b], Richard N. Zare[a,*], Richard G. Luthy[b]

[a]*Department of Chemistry, Stanford University, Stanford, California 94305-5080*
[b]*Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305-4020*

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Abstract

Microprobe two-step laser desorption/laser ionization mass spectrometry (μL^2MS) is used as a new analytical technique for the detection of polychlorinated biphenyls (PCBs). Three standard Aroclor solutions (Aroclor 1232, 1242, and 1262) and three samples of activated carbon spiked with Aroclor 1242 are examined. All the PCBs present in the Aroclor solutions are clearly identified using μL^2MS. The distribution of the peaks follows the relative natural abundances of the carbon and chlorine isotopes. μL^2MS analyses of the spiked particles of activated carbon reveal the presence of PCBs and an abundance of polycyclic aromatic hydrocarbons. The detection limit for PCBs on solid surfaces is determined to be between 1 and 10 ppm. Because the spatial resolution of the μL^2MS instrument varies between 10 and 40 microns, PCB information at the sub-particle scale can be obtained. (Int J Mass Spectrom 212 (2001) 41–48) © 2001 Elsevier Science B.V.

Keywords: Two-step laser mass spectrometry; Polychlorinated biphenyls; Microscale characterization

1. Introduction

Polychlorinated biphenyls (PCBs) have been used widely in industry as heat transfer fluids, hydraulic fluids, solvents, extenders, flame-retardants, organic diluents, and dielectric fluids. Such historic use has led to widespread release into the environment. Because PCBs are not easily biodegraded, they accumulate in natural food chains. A recent study of PCBs in butter produced in 23 countries has demonstrated the large-scale transport and bioaccumulation of this persistent organic compound [1]. PCBs have been implicated in a number of disease states, from infertility to carcinogenicity [2,3]. Presently, experts cannot agree on approaches to solve the problem of PCB bioaccumulation because of the interplay between complex physical and biological factors. PCBs are highly hydrophobic compounds and tend to bind strongly with soil or sediment particles. Some of the fundamental challenges in managing PCB-contaminated sediments include understanding how PCBs bind to different sediment components, how benthic organisms and particle feeders bioaccumulate PCB contaminants, what are the natural processes governing sediment-particle interactions and dispersion, and how bioavailable are PCBs bound to sediments.

Significant advances in recent decades have helped unravel the complexity of transfer of PCBs among

*Corresponding author. E-mail: zare@stanford.edu

Dedicated to R. Graham Cooks on the occasion of his sixtieth birthday.

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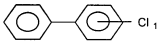
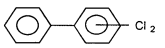
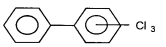
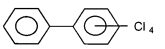
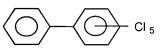
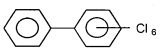
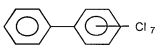
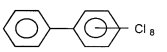
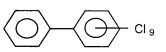
different trophic levels of an ecosystem [4]. Nevertheless, a major deficiency in understanding system functioning exists because of a lack of fundamental knowledge of physicochemical and biological complexity at the particle level. Specifically, we lack knowledge of how PCBs bind to different geochemical components of the sediment and how that affects the transfer of PCBs from sediment particles to the benthic feeders, and from there to higher organisms. Particle-scale availability of PCBs also affects the rates of natural attenuation through microbial processes and sequestration through burial processes. Thus, fundamental knowledge of PCB location and association with soil/sediment particles is key to unraveling the mechanism that governs the release from the sorbed state and accumulation in organisms.

Most PCB analytical techniques available to date, such as US EPA method 8082, rely on solvent extraction and analysis of bulk soil or sediment material [5]. These tests do not provide information on the particle-selective behavior of PCB binding. Recent work by Ghosh et al. [6] has illustrated the significance of understanding the nature of binding of polycyclic aromatic hydrocarbons (PAHs) to sediment particle classes. Their results showed that sediment from Milwaukee Harbor (USA) comprised two principal particle classes for PAHs, coal-derived and clay/silt, each having much different PAH levels, release rates, and desorption activation energies. PAH sorption on coal-derived particles is associated with slow release rates, and high desorption activation energies, whereas PAH sorption on clay/silt particles is associated with significant potential biodegradability, relatively fast release rates, and lower desorption activation energies [7]. These characteristics are attributed to fundamental differences in the organic matter to which the PAHs are sorbed. Although the majority of the PAHs are found preferentially on coal-derived particles, the PAHs on the clay/silt sediment fraction are more mobile and available, and thus potentially of greater concern. A similar microanalytical tool for in situ PCB abundance measurements at the sub-particle scale is therefore vital to understanding the fundamental nature of PCB binding and release from sediment particle classes.

Microprobe two-step laser desorption/laser ionization mass spectrometry (μL^2MS) was used for the in situ detection and microscale characterization of PAHs in the work on the Milwaukee Harbor Sediment mentioned previously. This technique is highly versatile and powerful. By making minor modifications to the experimental setup it is likely to be ideal for PCB analyses as well. Early, preliminary work on PCB detection was reported in the Ph.D. thesis of Clemett [8]; this study extends his effort. In the first step of μL^2MS, the output of a pulsed infrared (IR) laser is focused on the sample. This causes rapid heating in the spot area and thereby releases a plume of neutral molecules. In the second step, the output of a pulsed ultraviolet (UV) laser causes (1 + 1) resonance-enhanced multiphoton ionization of those desorbed molecules that are able to absorb this radiation and whose ionization potential is less than the energy of two photons at this wavelength. The resulting ions are then mass analyzed in a reflectron time-of-flight (TOF) mass spectrometer. The use of a laser to volatilize neutral molecules and the subsequent laser photoionization enables the in situ analysis of samples; and this procedure eliminates the sample preparation, extraction, purification, and separation steps that are involved in other techniques.

In a μL^2MS experiment, sampling occurs from a circular spot of micron dimensions. The surface being analyzed is visualized through a microscope objective that is connected to a video monitor. The exact size of the spot is determined by how tightly the IR laser beam can be focused onto the sample. This, in turn, depends primarily on the wavelength of the IR laser, its spatial beam properties, and the working distance of the microscope objective that is used to focus the beam. Depending on whether a CO_2 or Er:yttrium-aluminum-garnet (YAG) laser is used for desorption, the analysis spot of the current μL^2MS configuration has a diameter of 40 or 10 μ, respectively. By translating the sample under the microscope objective, it should be possible to generate spatial maps of the PCBs on the surface. Because a complete mass spectrum can be obtained from a single analysis spot, spatial maps of all the masses can be acquired simultaneously.

Table 1.
Structures of PCBs and composition of commercial aroclor mixtures 1232, 1242, and 1262

PCB	STRUCTURE	PERCENTAGE IN 1232	1242	1262
1. Monochlorobiphenyl		12	3	n.d.
2. Dichlorobiphenyl		28	13	n.d.
3. Trichlorobiphenyl		32	28	n.d.
4. Tetrachlorobiphenyl		24	30	n.d.
5. Pentachlorobiphenyl		4	22	1
6. Hexachlorobiphenyl		n.d.	4	27
7. Heptachlorobiphenyl		n.d.	n.d.	46
8. Octachlorobiphenyl		n.d.	n.d.	23
9. Nonachlorobiphenyl		n.d.	n.d.	3

n.d.: not detected

The objectives of the present work are to evaluate whether the μL^2MS technique is capable of identifying PCBs and to assess the utility of μL^2MS for in situ microscale detection of PCBs on heterogeneous sediment surfaces.

2. Experimental section

2.1. Samples

Aroclors 1232, 1242, and 1262 were obtained from Ultra Scientific, USA. The structures and approximate percents of the different PCBs in these samples are given in Table 1. The compositions of Aroclor 1232 and 1262 were determined by using gas chromatography with electron capture detection. Data for Aroclor 1242 was obtained from a study by Fiedler [9]. The solutions were prepared in hexane at a concentration of 100 μg/mL. Fifty microliters of each solution was evaporated on a glass plate for μL^2MS analysis. In addition, three samples of activated carbon were spiked with Aroclor 1242 at concentrations of 1, 10, and 100 ppm. This spiking was done by adding the appropriate amounts of Aroclor solution in hexane to the particles, and allowing the solvent to dry overnight.

2.2. Microprobe two-step laser desorption/laser ionization mass spectrometry technique

The μL^2MS instrument has been described in detail elsewhere [10,11]. The sample to be analyzed is placed on a brass platter that is 7 mm in diameter, and introduced into the instrument through a vacuum interlock. The instrument is evacuated to 2×10^{-8} Torr in 5 min. IR light from either a pulsed CO_2 (Alltech AL 853; 10.6 μm) or an Er:YAG laser (Big Sky Laser 571 A; 2.94 μm) is focused using a Cassegrainian microsocope objective, causing constituent molecules on the sample's surface to be desorbed. The IR laser power is kept low, $\sim 2.5 \times 10^6$ W/cm^2, to avoid plasma formation, minimize decomposition, and ensure the desorption of only neutral species. After an appropriate time delay (25 μs) during which the desorbed molecules move into the extraction region, the output from a pulsed Nd:YAG laser (Spectra Physics DCR11; 212 nm) intersects the gas plume causing only certain compounds to be selectively ionized. The 212 nm light is generated through frequency mixing of the Nd:YAG fundamental at 1.064 μm with the fourth harmonic at 266 nm in a barium borate crystal. The UV laser pulse intensity, $\sim 1.25 \times 10^6$ W/cm^2, is chosen to maximize parent ion signal whereas minimizing fragmentation. The ions produced are extracted from the source and injected into the reflectron TOF mass spectrometer using a series of charged plates in a modified Wiley–McLaren geometry [12]. A 20 cm^2 active area dual micro-channel plate detector is used in a Chevron configuation to detect the ions. The output of the detector passes through a fast preamplifier (LeCroy VV100BTB) and a timing filter (Ortec 474) and is displayed on a digital oscilloscope (LeCroy 9450). The

resulting signal is averaged in the oscilloscope with subsequent laser shots, and is transferred to a computer.

3. Results and discussion

3.1. Aroclor solutions

Fig. 1 shows the μL^2MS spectra (50-shot average) of solutions of Aroclor 1232, 1242, and 1262 evaporated on glass plates. The peaks marked correspond to the compounds listed in Table 1. Each PCB in the mixture is isotopically resolved as its parent ion. The PCB compounds have unique mass distributions that differ dramatically from those of PAHs and other compounds. This feature becomes particularly important when complex mixtures are examined because it is likely that other compounds with similar masses to those of the PCBs are present. There are some extra peaks, probably from contaminants, in the spectrum of Aroclor 1242.

Fig. 2 presents the spectra predicted for dichloro-, tetrachloro-, and heptachloro-biphenyls based on values of the natural abundances of the chlorine and carbon isotopes. These spectra are compared with corresponding μL^2MS spectra. The results indicate that the peak distributions that we obtain experimentally are very similar to the ones expected, implying that the integrity of the isotopic ratios is retained during μL^2MS analyses.

From Fig. 1 it is evident that μL^2MS detects all the PCB congeners of one mass in a single peak. In most of the conventional techniques used for PCB analysis, the isomers of a given PCB series are chromatographically separated. For molecules with large number of isomers, however, the separation effectively lowers the detection sensitivity. μL^2MS does not face a similar problem. In an ideal situation it would be beneficial to use μL^2MS in tandem with some technique that gives clear isomer separation and identification. The complementary information obtained would provide a complete understanding of the PCBs present in the sample.

The prominent PCBs identified in Aroclor 1232, 1242, and 1262 during μL^2MS analysis [Fig. 1] are consistent with the information in Table 1. μL^2MS is not used to obtain quantitative information on the relative abundances or absolute concentrations of compounds present in a sample. This is because the intensities of μL^2MS peaks are not only a reflection of the concentration of the compound in the sample but also depend on the volatility and the photoionization cross section of the species at a particular laser ionization wavelength. The photoionization cross sections of different PCBs have not been characterized for our instrument as yet.

Some experiments were performed using 266 nm light for photoionization as well. PCBs were identified even at this longer wavelength, but the signal intensity markedly dropped. This signal decrease results from PCB molecules being more readily resonantly photoionized by the more energetic photons at 212 nm.

3.2. Samples of activated carbon spiked with Aroclor 1242

Particles of activated carbon were spiked with Aroclor 1242 to determine the effect of the substrate in μL^2MS analysis of PCBs. Activated carbon was chosen because it is well known that PCBs bind very strongly to this material, and it is likely that PCBs bind to soils and sediments in a similar manner.

Fig. 3 shows the μL^2MS spectrum of activated carbon particles spiked with 10 ppm of Aroclor solution. The spectrum is, once again, a 50-shot average, and the sample was repositioned between laser shots so that desorption occurred from a fresh portion of the surface every time. Two distinct mass envelopes appear, one corresponding to PAHs of lower molecular weight and the other corresponding to the PCBs added. The main PAHs present include naphthalene (128 Da), acenaphthene (154 amu), phenanthrene/anthracene (178 Da), and their alkylated counterparts and the PCBs marked in the spectrum correspond to the ones mentioned in Table 1. Although PAHs are not expected to be present in pure activated carbon, this particular sample may have been exposed to laboratory air for an extended period resulting in sorption of some of the volatile PAHs.

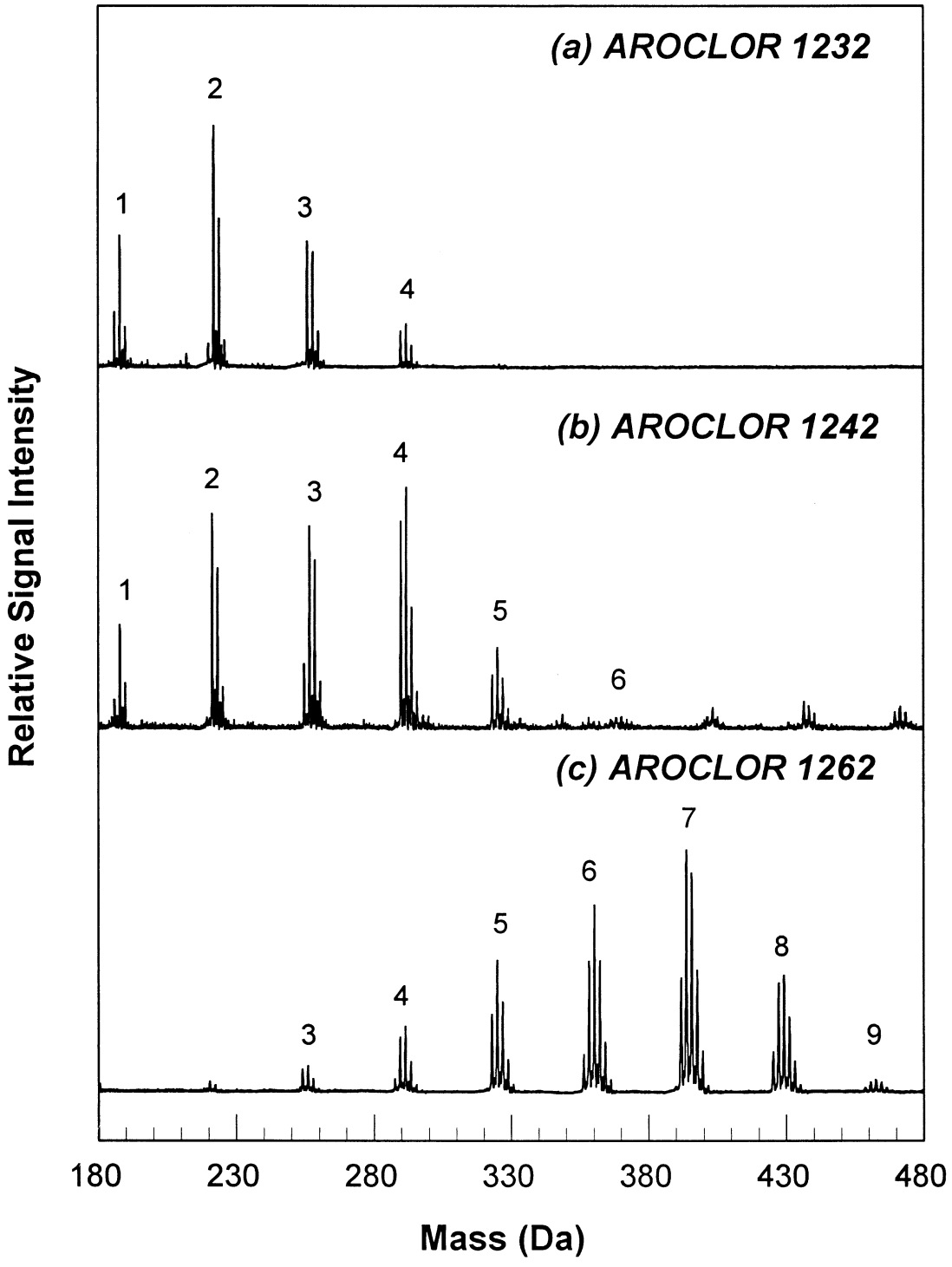


Fig. 1. μL^2MS spectra of the PCB mixtures (a) Aroclor 1232, (b) Aroclor 1242, and (c) Arocolor 1262.

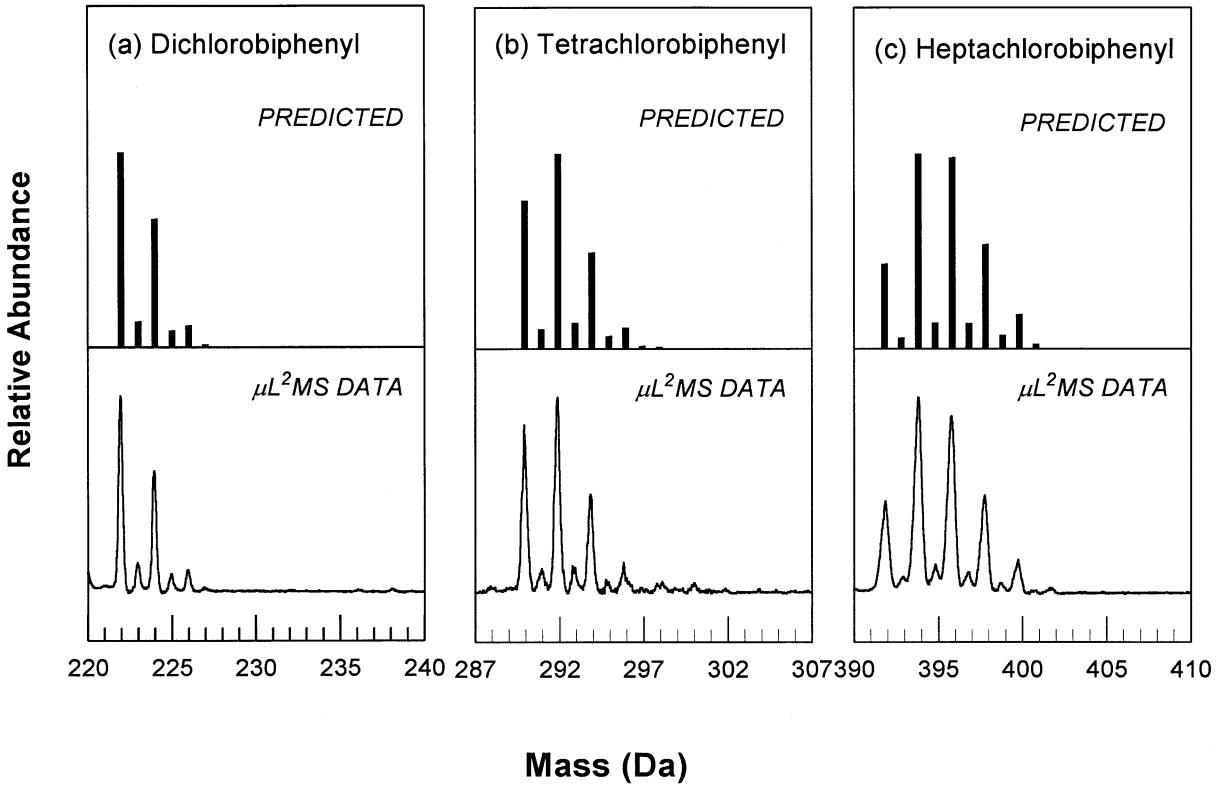


Fig. 2. Predicted peak distributions and corresponding μL^2MS spectra of (a) dichlorobiphenyl, (b) tetrachlorobiphenyl, and (c) heptachlorobiphenyl. The appropriate regions of Fig. 1 were expanded to depict the experimental data.

The presence of PCB peaks in spectra of the activated carbon particles demonstrates the feasibility of using μL^2MS to detect PCBs bound to solid substrates. The PCB peak distribution for this sample differs from that of the Aroclor solution evaporated on a glass plate [Fig. 1(b)]. Higher molecular weight PCBs, such as the tetrachloro- and pentachloro- biphenyls, seem to bind more strongly to the solid substrate than ones of lower molecular weight.

In Fig. 3 the μL^2MS signal intensity for the PAHs is much greater than that for the PCBs. This difference implies that the instrument is either much more sensitive to PAHs than PCBs, or activated carbon sample is richer in PAHs than PCBs. We routinely use 266 nm of photoionization light for PAHs. It is not surprising that we see these compounds even at 212 nm because it is known that the intermediate excited state of PAHs, that corresponds to a $\pi \rightarrow \pi^*$ transition, typically has two broad multimodal distributions in the 210–230 and 260–280 nm wavelength ranges. The extinction coefficients for the shorter wavelength transition tend to be larger, and so photoionization at 212 nm offers a greater sensitivity to PAHs. The fact that the shorter wavelength reduces the species selectivity of the ionization event may compromise the ease of μL^2MS spectral analyses in some situations. Fortunately, PCBs have such distinct peak distributions during μL^2MS analysis that we can confidently identify them in complex spectra.

In order to determine the detection sensitivity of the μL^2MS technique, two additional activated carbon samples spiked with 100 and 1 ppm of PCBs were analyzed. For 100 ppm particles, distinct PCB peaks are present. At 1 ppm, the μL^2MS spectrum still shows the PCB peaks, but the signal/noise ratio drops below the detection limit. Thus, we conclude that the

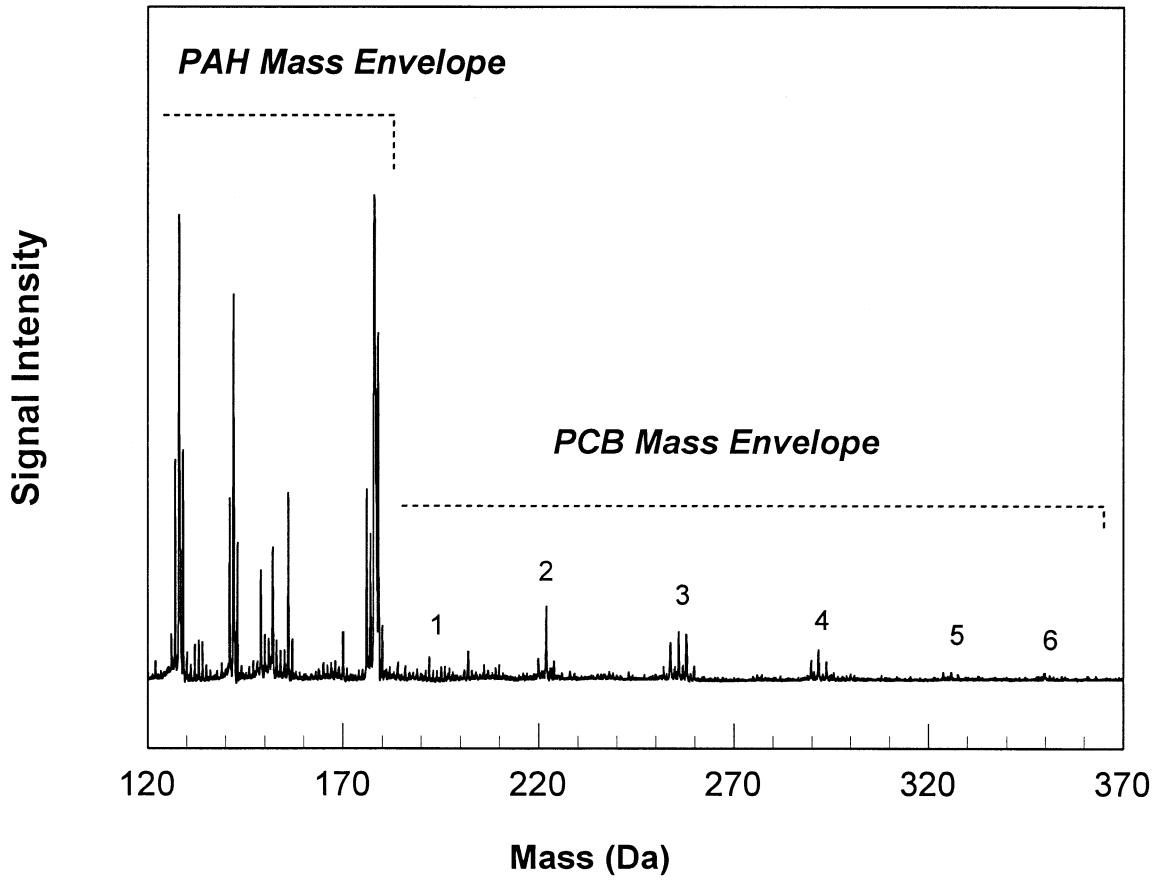


Fig. 3. μL^2MS spectrum of activated carbon particles spiked with 10 ppm of Aroclor 1242.

detection limit for our current experimental setup is in the range of 1 to 10 ppm. The uniform decrease in μL^2MS signal as we go from a highly concentrated sample to one with trace amounts of PCBs implies that semi-quantitative analysis of relative PCB abundance on different particles in a sample may be assessed using the μL^2MS technique.

4. Conclusions

The μL^2MS technique is a very powerful and highly versatile microanalytical technique that has successfully been used to study a wide range of compounds such as PAHs [13–22], fullerenes [8,23], porphyrins [24], dyes [25,26], amino acids [27], and polymer additives [28,29]. In this study we extend the capabilities of μL^2MS to detect PCBs.

Using 212 nm light for photoionization, PCBs were identified in the three Aroclor solutions examined. The PCB molecules have distinct signatures in the μL^2MS spectra, which are unique for the PCB compound being examined and differ dramatically from PAHs or other compounds likely to be present in soils and sediments. The results of the experiments in which activated carbon particles were spiked with PCBs indicate that μL^2MS is a feasible technique for PCB detection on solid substrates. Furthermore, the detection sensitivity of the current μL^2MS configuration for PCBs is determined to be between 1 and 10 ppm. With this capability to detect PCBs, future work

can be carried out to establish what correlations exist between PCB location on a sediment particle and the type of organic matter present.

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References

[1] O.I. Kalantzi, R.E. Alcock, P.A. Johnston, D. Santillo, R.L. Stringer, G.O. Thomas, K.C. Jones, Environ. Sci. Technol. 35 (2001) 1013.
[2] United States Environmental Protection Agency, Doc. No. EPA 440/5-90-068, Office of Water, Washington, DC, 1980.
[3] United States Enviornmental Protection Agency, Doc. No. EPA-823-F-99-019, Office of Water, Washington, DC, 1999.
[4] J.W. Nichols, C.P. Larsen, M.E. McDonald, G.J. Niemi, G.T. Ankley, Environ. Sci. Technol. 29 (1995) 604.
[5] United States Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Office of Solid Waste, Washington, DC, 2000.
[6] U. Ghosh, J.S. Gillette, R.G. Luthy, R.N. Zare, Environ. Sci. Technol. 34 (2000) 1729.
[7] J.W. Talley, U. Ghosh, S.G. Tucker, J.S. Furey, R.G. Luthy, Environ. Sci. Technol., in press.
[8] S.J. Clemett, Ph.D. thesis, Stanford University, Stanford (1996).
[9] H. Fiedler, Proceedings of the UNEP Regional Awareness Raising Workshop on Persistent Organic Pollutants, Abu Dhabi, United Arab Emirates, 1998.
[10] S.J. Clemett, R.N. Zare, in Molecules in Astrophysics: Probes and Processes, E.F. Dishoeck (Ed.), Leiden, Netherlands, 1997, p. 305.
[11] R. Zenobi, R.N. Zare, in Advances in Multiphoton Processes and Spectroscopy, S.H. Lin (Ed.), World Scientific, Singapore, 1991, Vol. 7, p. 1.
[12] W.C. Wiley, I.H. McLaren, Rev. Sci. Instrum. 26 (1955) 1150.
[13] R. Zenobi, J.M. Philippoz, P.R. Buseck, R.N. Zare, Science 246 (1989) 1026.
[14] D.S. McKay, E.K. Gibson, K.L. Thomas-Keprta, H. Vali, C.S. Romanek, S.J. Clemett, X.D.F. Chillier, C.R. Maechling, R.N. Zare, Science 273 (1996) 924.
[15] L.J. Kovalenko, C.R. Maechling, S.J. Clemett, J.M. Phillipoz, R.N. Zare, C.M.O.D. Alexander, Anal. Chem. 64 (1992) 682.
[16] S.J. Clemett, C.R. Maechling, R.N. Zare, P.D. Swan, R.M. Walker, Lunar and Planet. Sci. XXIV (1993) 309.
[17] M.J. Dale, A.C. Jones, S.J.T. Pollard, P.R.R. Langridge-Smith, Analyst 119 (1994) 571.
[18] M.J. Dale, A.C. Jones, S.J.T. Pollard, P.R.R. Langridge-Smith, A.G. Rowley, Environ. Sci. Technol. 27 (1993) 1693.
[19] J.S. Gillette, R.G. Luthy, S.J. Clemett, R.N. Zare, Environ. Sci. Technol. 33 (1999) 1185.
[20] S.M. Hankin, P. John, Anal. Chem. 71 (1999) 1100.
[21] O.P. Haefliger, T.D. Bucheli, R. Zenobi, Environ. Sci. Technol. 34 (2000) 2178.
[22] Q. Zhan, P. Voumard, R. Zenobi, Rapid Commun. Mass Spectrom. 9 (1995) 119.
[23] L. Becker, T.E. Bunch, L.J. Allamandola, Nature 400 (1999) 227.
[24] M.J. Dale, K.F. Costello, A.C. Jones, P.R.R. Langridge-Smith, J. Mass Spectrom. 31 (1996) 590.
[25] M.J. Dale, A.C. Jones, P.R.R. Langridge-Smith, K.F. Costello, P.G. Cummings, Anal. Chem. 65 (1993) 793.
[26] M.J. Dale, Q. Zhan, R. Zenobi, K. Costello, P.R.R. Langridge-Smith, Anal. Methods Instrum. 2 (1995) 101.
[27] F. Engelke, J.H. Hahn, W. Henke, R.N. Zare, Anal. Chem. 59 (1987) 909.
[28] Q. Zhan, R. Zenobi, S.J. Wright, P.R.R. Langridge-Smith, Macromolecules 29 (1996) 7865.
[29] S.J. Wright, M.J. Dale, P.R.R. Langridge-Smith, Q. Zhan, R. Zenobi, Anal. Chem. 68 (1996) 3585.