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## DIRECT ANALYSIS OF ORGANIC PRIORITY POLLUTANTS BY IMS

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### ABSTRACT

Many routine methods for monitoring of trace amounts of atmospheric organic pollutants consist of several steps. Typical steps are: (1) **collection** of the air sample, (2) **trapping** of organics from the sample, (3) **extraction** of the trapped organics, and (4) **identification** of the organics in the extract by GC (gas chromatography), HPLC (High Performance Liquid Chromatography), or MS (Mass Spectrometry). These methods are often cumbersome and time consuming. A simple and fast method for monitoring atmospheric organics using an IMS (Ion Mobility Spectrometer) is proposed. This method has a short sampling time and does not require extraction of the organics since the sample is placed directly in the IMS. The purpose of this study was to determine the responses in the IMS to organic "priority pollutants." Priority pollutants including representative polycyclic aromatic hydrocarbons (PAHs), phthalates, phenols, chlorinated pesticides, and polychlorinated biphenyls (PCBs) were analyzed in both the positive and negative detection mode at ambient atmospheric pressure. Detection mode and amount detected are presented.

### INTRODUCTION

Our research group has, for several years, been detecting and quantitating organic pollutants, particularly anthropogenic ones, in very clean (open ocean) air at very low concentrations, picograms or less.<sup>1-4</sup> Very often, this analysis would require collection of large volumes of air using trapping materials for these organics, such as adsorbents like Amberlite and Florisil, followed by extraction of the trapped organics and then identification and quantitation by GC-ECD and GC-MS. This is a cumbersome, tedious, time consuming process and often contaminants are introduced into the samples. When we were kindly provided with a PCP IMS 100 by the FAA for explosive analysis, we took the opportunity to determine the scope and limitations of IMS (ion mobility spectrometry) as a faster way of direct analysis of real-time, real-life air samples. In order to see if IMS is suitable for detecting priority pollutants, we needed to first screen these compounds. Although detection of organics using IMS has been carried out for a number of years, often the reports in the literature are incomplete and usually the IMS operating conditions vary from report to report.

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The goal of this research is to develop a fast and simple method for monitoring atmospheric organic priority pollutants using IMS. The objective for this study was to determine if different classes of semi-volatile organic priority pollutants give an IMS response. There are 128 priority pollutants, of these 110 are organic compounds, 80 of which are semi-volatile organics. We have analyzed over 90% of the semi-volatile organic priority pollutants. The IMS response for each compound studied was determined at atmospheric pressure in the negative detection mode with nitrogen and the positive detection mode with air. This paper will present an overview of general IMS responses for the different classes. Subsequent publications will emphasize methods that can be used to distinguish the different pollutants, reduced mobilities of the semi-volatile priority pollutants (studies are continuing to determine the purity of the compounds and peaks in the spectra due to impurities), and the use of IMS in monitoring atmospheric organics.

## **EXPERIMENTAL METHODS**

IMS spectra of individual organic pollutants were obtained using a PCP-100 (from PCP, Inc., 2155 Indian Road, West Palm Beach, Florida, 33409-3287) and the instruments instructions, including the use of its sample holder (a quartz tube 4.0 mm + 0.4 mm i.d. x 1.5" long, with a small plug of glass wool). IMS conditions for both modes were: IMS temperature of 200°C, polarity of 3000 volts, drift flow of 600 ml/min, carrier flow of 400 ml/min and atmospheric pressure. For the negative detection mode, negative polarity, nitrogen and a delay of 2000 us were used. For the positive detection mode, positive polarity, air and a delay of 6000 us were used.

U.S. EPA Standards (100-500 ng/ul) in methanol were diluted to provide concentrations of 50 ng/ul. 2-4 ul of the diluted solution were placed in the IMS quartz sample holder; after the solution had evaporated (30 seconds), the sample holder was placed in the IMS. Detection limits vary from low nanograms to 400 ng. Any compound requiring more than 400 ng was considered unresponsive to IMS.

## **RESULTS AND DISCUSSION**

Results are summarized in Table 1. The major findings were as follows. All of the PAHs investigated were detectable only in the positive mode. PAHs were very responsive even at low amounts. The phenols were detected only in the negative mode with the exception of 2,4-dimethylphenol which was only detected in the positive mode. Most of the phenols were very

responsive in the negative mode even at low amounts. In general, the ubiquitous PCBs were detected in the negative mode with the exception of PCB 1221, which was detected in both modes. A prominent chloride peak was observed in the negative mode with nitrogen for all of the PCBs analyzed. IMS spectra of the PCBs contained several peaks. This could be expected since PCB mixtures may contain as many as several hundred isomers. The ubiquitous phthalates were detected in both the positive and negative modes. However, phthalate detection was more sensitive in the positive mode.

Most of the chlorinated pesticides were detected in both modes with the exception of aldrin, heptachlor epoxide and toxaphene which were detected only in the negative mode. Most of these highly chlorinated compounds gave a large chloride peak in the negative mode. Many of the compounds gave more than one peak indicating one or more product ions from the parent molecule as well as the chloride ion.

IMS analysis of some of these compounds using different operating conditions have been reported by other researchers<sup>5-12</sup>. Published results were similar to our findings for phenanthrene<sup>6,8</sup>, fluoranthene<sup>6,8,9,12</sup>, dimethyl phthalate<sup>5,7,11,12</sup>, chrysene<sup>5,7</sup>, diethyl phthalate<sup>7,11</sup>, fluorene<sup>9,12</sup>, dieldrin<sup>12</sup>, and 2,4-dichlorophenol.<sup>10</sup> Reported results for dibutyl phthalate<sup>11</sup>, anthracene<sup>8,9,12</sup>, endrin<sup>12</sup>, and acenaphthalene<sup>8</sup> differed from our findings but may have been due to a difference in IMS operating conditions.

Experiments are continuing to obtain IMS spectra and reduced mobilities for the remaining semi-volatile organic priority pollutants. Once these experiments have been completed, field studies using the IMS air sampling and detection method will be conducted.

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**TABLE 1. Summary of IMS Responses of the Different Priority Pollutant Classes**

PRIORITY POLLUTANT	AMOUNT DETECTED (nanograms)	
	POSITIVE MODE	NEGATIVE MODE
<b>Polycyclic Aromatic Hydrocarbons</b>		
Acenaphthene	200	ND
Acenaphthylene	100	ND
Anthracene	25	ND
Chrysene	100	ND
Fluoranthene	50	ND
Fluorene	100	ND
Phenanthrene	100	ND
Pyrene	100	ND
<b>Phenols</b>		
2-Nitrophenol	ND	ND
4-Nitrophenol	ND	100
2,4-Dichlorophenol	ND	200
2,4-Dimethylphenol	400	ND
2,4-Dinitrophenol	ND	100
2,4,6-Trichlorophenol	ND	100
Pentachlorophenol	ND	50
<b>Polychlorinated Biphenyls</b>		
PCB 1221	400	400
PCB 1242	ND	400
PCB 1254	ND	100
PCB 1260	ND	100
<b>Phthalates</b>		
Butyl Benzyl Phthalate	50	200
Di-n-butyl Phthalate	50	400
Di(2-ethylhexyl) Phthalate	50	200
Diethyl Phthalate	25	400
Dimethyl Phthalate	50	400
Di-n-octyl Phthalate	50	200
<b>Chlorinated Pesticides</b>		
Aldrin	ND	100
Chlordane	150	100
Dieldrin	100	100
Endosulfan Sulfate	200	100
Endrin	250	100
Endrin Aldehyde	400	100
Heptachlor	250	300
Heptachlor Epoxide	ND	200
Toxaphene	ND	100

ND = Not detected, > 400 ng