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# Analysis of Impregnated Charcoals by Desorption Ionization Mass Spectrometry

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**The desorption ionization (DI) mass spectrometric methods, secondary ion mass spectrometry (SIMS), and fast-atom bombardment mass spectrometry (FABMS) have been used for the analysis of adsorbates and impregnants on charcoals. Charcoal samples were prepared for analysis by either mounting on silver substrates (SIMS) or slurrying with glycerol (FABMS). Specificity was achieved by derivatization of the target species on the charcoal. The enhanced sensitivity for precharged organic species in DI mass spectrometric methods was exploited by derivatization of the target compound to form quaternary ammonium salts. Metal salt impregnated samples were derivatized for metal analysis by chelation. The SIMS and FABMS techniques proved to be simple and rapid methods for the direct qualitative analysis of impregnated charcoals.**

Activated carbons or charcoals are used widely as adsorbents for airborne or aqueous pollutants. The analysis of charcoals for adsorbed species typically involves solvent extraction followed by separation and identification of the extract components, often with a combined chromatographic/mass spectrometric method (e.g., GC/MS) (*1*, *2*). Thermal desorption of adsorbates from charcoals followed by mass spectrometric identification has been shown to be an effective method also (*3*, *4*). Certain nonvolatile or thermally labile compounds are difficult to analyze by using these methods but are more amenable to the newer, "softer" ionization techniques. The objective of this research is to use the desorption ionization (DI) mass spectrometric techniques, secondary ion mass spectrometry (SIMS), and fast-atom bombardment mass spectrometry (FABMS), for the direct analysis of adsorbates on charcoal.

Traditionally, SIMS has been used for the characterization of solid surfaces (i.e., elemental analysis and depth profiling) (*5*). The use of low primary beam current densities in static or molecular SIMS (*6*) allows the detection of intact organic molecular ions from overlayers on solid, usually metallic, surfaces (*7–9*). Charcoal and graphite have been used as sample substrates for organic molecular SIMS analyses (*10*, *11*). These latter studies have taken advantage of the unique nature of carbon; it is a strong organic adsorbent even under high-vacuum conditions, long-lived molecular ion emission is observed under intense particle bombardment ($10^{-6}$–$10^{-7}$ A/cm$^2$), and the carbon substrate does not contribute significantly to the background.

The subject of this report is the study of charcoals that contain impregnants and adsorbates that are required by their applications. In addition to SIMS analyses, FABMS (*12*), a relatively recent offshoot of SIMS, was investigated. The FABMS technique offers the possibility of in situ extraction of the charcoal in the liquid matrix followed by desorption and mass analysis of the extracted compounds from the liquid substrate.

The analytical utility of SIMS and FABMS for the qualitative analysis of charcoal adsorbates will be demonstrated by use of three selected charcoal samples. These samples were chosen to highlight the advantages of DI mass spectrometry.

## EXPERIMENTAL SECTION

Charcoal I was a 5% triethylenediamine (TEDA), or 1,4-diazabicyclo[2.2.2]octane, impregnated coal-base charcoal. Charcoal II was a coal-based charcoal impregnated (~1%) with metal salts of copper and chromium as ammoniacal solutions of $CuCO_3$ and $K_2CrO_4$. These impregnated charcoals were prepared by spraying appropriate solutions onto charcoal beds. Charcoal III was a coconut shell charcoal onto which a mixture of Girard's reagent P, 1-(carboxymethyl)pyridinium chloride hydrazide (~10 mg/100 mg of charcoal), and acetic acid (~1 μL/100 mg of charcoal) had been adsorbed from solution. Air containing ~10 ppm concentration of acetone was drawn over charcoal III (~100 mg) at a rate of ~50 mL/min for 60 min. The charcoal was exposed to a maximum of 3.6 μL of acetone (~3% by weight acetone/charcoal).

The SIMS instrument used was a double-focusing mass spectrometer that has been described previously (*13*). The SIMS experiments were performed by burnishing approximately 1–5 mg of charcoal onto a piece of acid-etched silver and bombarding the sample with a 3-keV $Ar^+$ or $Xe^+$ beam of ~$10^{-7}$ A/cm$^2$ current density. The FABMS experiments were performed with a VG Analytical ZAB-2F mass spectrometer. The samples were prepared by making a slurry of approximately 10 mg of the charcoal with glycerol. The sample was analyzed by bombarding it with an 8–10 keV $Xe^0$ beam of ~$10^{-4}$ A/cm$^2$ current density. The glycerol matrix ions were subtracted from the FABMS spectra to simplify the data presentation. All mass spectra shown are single scan spectra.

## RESULTS AND DISCUSSION

Charcoal I, which was impregnated with TEDA, is used in the nuclear industry for the trapping of atmospheric radioactive iodide as methyl iodide. TEDA has been found to prolong the service lifetime of such charcoals in high-humidity environments (*14*). This sample was chosen as an example of a charcoal with an impregnant that reacts with an airborne contaminant and where the charcoal is analyzed before and after service exposure.

The SIMS results of charcoal I are presented in Figure 1. Each spectrum is normalized to the most abundant ion in the corresponding spectrum. Figure 1a shows the spectrum of TEDA-impregnated charcoal on silver. In addition to the silver ions $[Ag]^+$ (*m/z* 107 and 109), the protonated molecule (*m/z* 113) of TEDA is observed.

It had been speculated that methyl iodide and TEDA react on the charcoal surface to form a quaternary ammonium salt (Figure 2), but no direct evidence had been obtained previously (*14*). With this in mind, the TEDA–$CH_3I$ salt was synthesized by adding an excess of $CH_3I$ to a solution of TEDA in methanol, and the salt was crystallized from solution. The SIMS spectrum of this salt deposited from solution onto silver is shown in Figure 1b. The $[TEDA + CH_3]^+$ (*m/z* 127) species and the $[TEDA + 2CH_3 - H]^+$ (*m/z* 141) species were observed with a combined ion abundance that was approximately 10 times greater than that for the protonated molecule from the TEDA-impregnated charcoal (Figure 1a). The TEDA-impregnated charcoal then was exposed to $CH_3I$ by passing

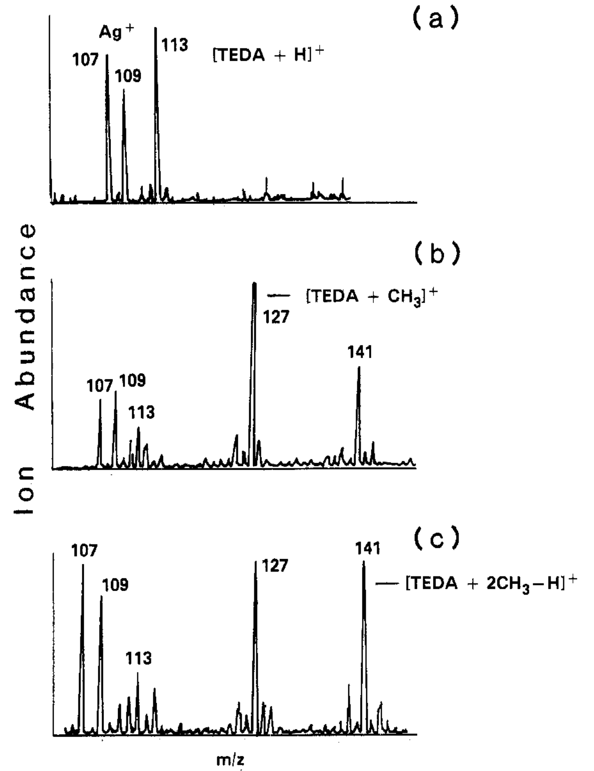


**Figure 1.** Secondary ion mass spectra of (a) TEDA-impregnated charcoal (I), (b) TEDA·$CH_3I$ salt, and (c) TEDA-impregnated charcoal (I) after exposure to $CH_3I$ vapor.

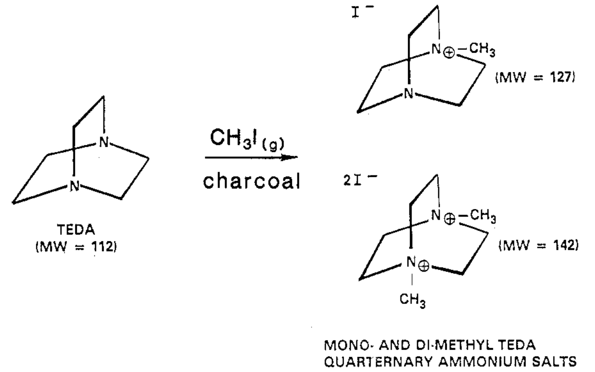


**Figure 2.** Reaction of TEDA with $CH_3I$ on the charcoal surface to form quaternary ammonium salts.

this vapor in nitrogen over a bed of the charcoal. This sample was analyzed and the SIMS spectrum is shown in Figure 1c. The spectra in Figure 1b,c are similar; the relative abundances of $m/z$ 127 and 141 were found to change depending on the method of sample preparation. The FABMS experiments yielded similar results in that $m/z$ 127 and 141 were the most abundant analyte ions. These experiments confirm that the TEDA–$CH_3I$ quaternary ammonium salt is formed upon exposure of a TEDA-impregnated charcoal to methyl iodide.

Of fundamental importance to the industrial application is that both nitrogens on the TEDA molecule react with $CH_3I$ forming the diquaternary ammonium salt (i.e., 2 mol of $CH_3I$/mol of TEDA). In addition to the observation of the $m/z$ 141 ion, evidence of the diquaternary ammonium salt was provided by the observation of the $[TEDA + 2CH_2 + I]^+$ ($m/z$ 269) species which was ~17% of the abundance of the $[M + CH_3]^+$ ion. Furthermore, the doubly charged molecular ion $[TEDA + CH_3 + CD_3]^{2+}$ ($m/z$ 72.5) has been observed in the SIMS spectrum of the deuterium-labeled $CD_3I$–TEDA–$CH_3I$ salt (*15*). This salt was synthesized by adding $CD_3I$ to an excess of TEDA, purifying the TEDA–$CD_3I$ salt, and finally, reacting this salt with $CH_3I$. The deuterated analogue was used so that a doubly charged ion at half mass was generated allowing unambiguous detection at low resolving power. Diquaternary ammonium salts have been the subject of recent studies (*16–18*). In these studies, doubly charged TEDA salt species have not been identified in the mass spectra.

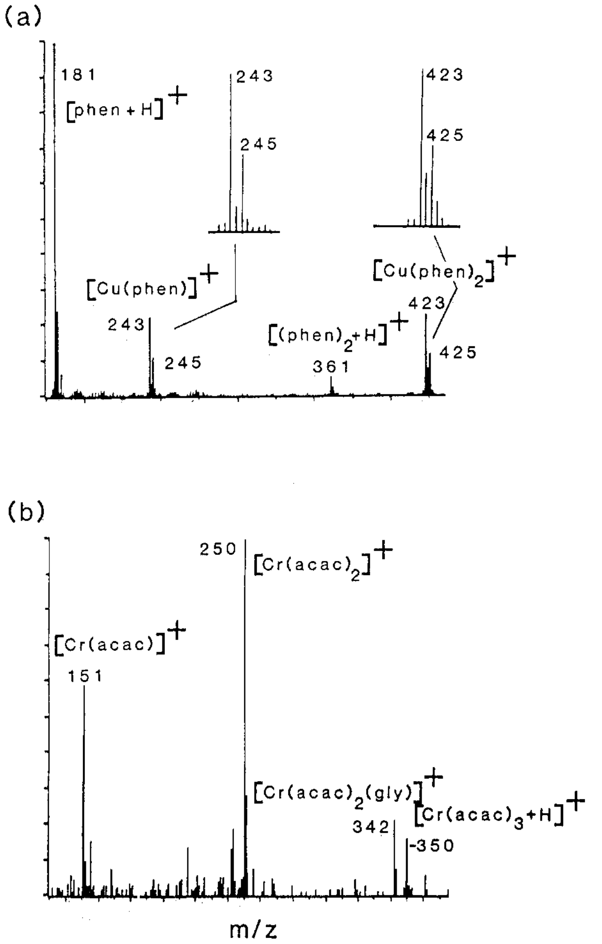


**Figure 3.** The FABMS spectra of metal salt impregnated charcoal (II): (a) in glycerol and 1,10-phenanthroline (phen); (b) in glycerol and 2,4-pentanedione (acac).

The derivatization of the TEDA-impregnated charcoal with $CH_3I$ to form the quaternary ammonium salt is especially advantageous when the charcoal is impregnated at low levels (<1%) (i.e., when sensitivity is a problem) because the positive ion yield of a quaternary ammonium salt is usually greater than that of the underivatized organic compound (*19*). This concept of derivatization for a specific target compound functionality was pioneered by Cooks et al. (*20*) and is being exploited and studied further in this laboratory (*15*).

Activated charcoals that are used for scavenging of atmospheric pollutants are often impregnated with compounds such as metal salts to enhance their trapping efficiency. Each of the two metal salts impregnated into charcoal II was selectively chelated with appropriate complexing agents. The compound 1,10-phenanthroline was chosen to complex copper selectively. Chromium was analyzed selectively by chelation with a β-diketone, 2,4-pentanedione (acac), to form the chromium β-diketonates, $Cr(acac)_n$ ($n$ = 1, 2, 3). Similar complexes have been studied previously by SIMS (*21, 22*).

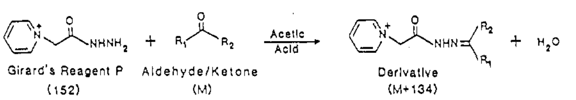
The FABMS spectra of charcoal II in glycerol after addition of the chelating agents are shown in Figure 3. Analytically useful information could not be obtained from the FABMS spectrum of charcoal II alone in glycerol. The SIMS of the charcoal alone did not allow the detection of $Cr^+$ and $Cu^+$ except with high primary current densities (~$10^{-6}$ A/$cm^2$)

which yielded low abundances of the analyte ions. The addition of 1,10-phenanthroline (phen) to the charcoal/glycerol mixture yielded the spectrum in Figure 3a. The most abundant ion is the protonated molecule of phenanthroline [phen + H]$^+$ ($m/z$ 181), and the copper-phenanthroline complex ions, [Cu(phen)]$^+$ ($m/z$ 243 and 245) and [Cu(phen)$_2$]$^+$ ($m/z$ 423 and 425), are observed also. Figure 3b shows the FABMS spectrum obtained after the addition of 2,4-pentanedione (acac) to the charcoal II/glycerol mixture. Chromium-acac complex ions, [Cr(acac)]$^+$ ($m/z$ 151), [Cr(acac)$_2$]$^+$ ($m/z$ 250), and [Cr(acac)$_3$ + H]$^+$ ($m/z$ 350), are observed. Mixed ligand complexes such as [Cr(acac)(phen)]$^+$ ($m/z$ 331) and [Cr(acac)$_2$(phen)]$^+$ ($m/z$ 430) are observed also when both chelates are added to the charcoal/glycerol slurry.

The charcoal/glycerol/chelating agent slurry could be analyzed within 5–10 min after mixing. Increased metal chelate ion abundances were observed when the slurry was allowed to stand for longer periods of time (30–60 min) and when the probe temperature was increased (ambient to ~70 °C). In addition, the phenanthroline complexation scheme has been used to analyze silver from an impregnated charcoal used for water treatment from which silver-phenanthroline complex ions [Ag(phen)]$^+$ and [Ag(phen)$_2$]$^+$ are observed. Metal-impregnated charcoals were mixed with solutions of the chelating agents and then analyzed from silver by SIMS yielding results similar to those from the FABMS experiments. The advantage of the FABMS method is the in situ extraction/complexation of the target species. Unfortunately, the oxidation state of the metal cannot be determined from the mass spectra. The phenanthroline complexes of Cu(I) and Cu(II) give nearly identical spectra. The oxidation state of the metal may be changed during the desorption process.

Charcoal III contained Girard's reagent P, a compound that has been used for making water-soluble derivatives of aldehydes and ketones (*23*). Because Girard's reagent P is a quaternary ammonium salt, the analysis of derivatives using this compound is ideally suited for DI mass spectrometry. We are evaluating the use of Girard's reagent P as a derivatizing agent for a wide variety of aldehydes and ketones (*15*). The derivatization of aldehydes and ketones by other reagents for SIMS analysis has been discussed (*20*).

Charcal III is an example of impregnating an adsorbent with a derivatizing agent specific for airborne compounds having a carbonyl group. Girard's reagent P reacts with the carbonyl-containing compounds according to reaction 1. The ions corresponding to the derivatized carbonyl-containing compounds are detected as [M + 134]$^+$, where M is the molecular weight of the aldehyde or ketone. The SIMS spectrum of charcoal III impregnated with the derivatizing reagent before exposure to acetone is shown in Figure 4a. The ions observed are those of the Girard's reagent P including the molecular ion ($m/z$ 152) and a fragment ion ($m/z$ 120) corresponding to loss of $N_2H_4$ to form the ketene ion.



(1)

The SIMS spectrum of this charcoal after exposure to the 10 ppm acetone in air is shown in Figure 4b, where the derivatized acetone ion ($m/z$ 192) and a fragment ion ($m/z$ 113) corresponding to loss of pyridine from the derivative ion are observed. The underivatized adsorbed ketones or aldehydes are not observed easily with SIMS. This is the first report of adsorbing Girard's reagent P on charcoal for atmospheric trapping of airborne contaminants. The absolute detection and saturation limits of this method have not been determined and these will depend upon charcoal surface area, compound reactivities, etc. Further research is required to completely evaluate the analytical utility of this technique.

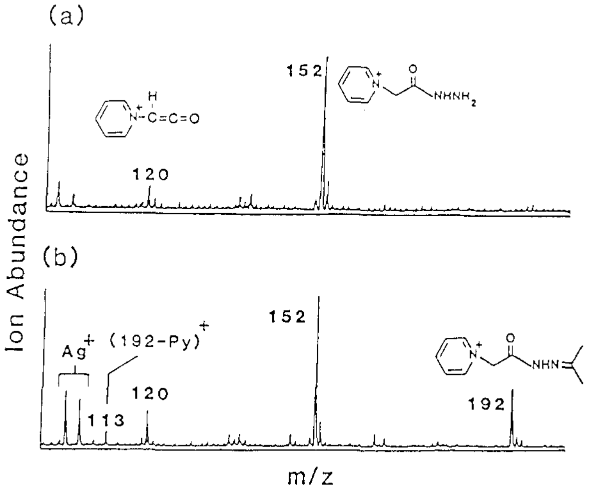


**Figure 4.** Secondary ion mass spectra of (a) Girard's reagent P impregnated charcoal (III) and (b) Girard's reagent P impregnated charcoal (III) after exposure to ~10 ppm acetone in air.

The Girard's reagent P derivatization scheme has also been used in impinger sampling of air contaminated with acrolein (2-propenal). The derivatization reagent was dissolved in an ethanol/water solution with a small amount of acetic acid to a total volume of 10 mL in the impinger. Air was drawn through the derivatizing solution by a pump for 2 h, followed by analysis of 1 μL of the solution by SIMS. The derivatives of acrolein (molecular weight 56 + 134 = $m/z$ 190) and other related aldehydes were detected (*15*).

## CONCLUSIONS

These examples demonstrate the utility of DI mass spectrometric methods for the direct and rapid qualitative analysis of adsorbates and impregnants on charcoals. Because of the complex nature of some carbonaceous materials, such as airborne particulate matter or soot, DI mass spectrometry may not identify and quantify every adsorbate on the carbon as the extraction/GC/MS procedure can. However, by employing derivatization methods to selectively "label" a target compound or functionality, thereby enhancing the detection of a class of compounds over others in the matrix, DI mass spectrometry is a rapid alternative to the more time-consuming separation techniques.

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# Quantitative Determination of Paint Additives with Fast Atom Bombardment Mass Spectrometry

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**Quantitative fast atom bombardment (FAB) mass spectrometry methods were investigated for the analysis of the photostabilizer bis(2,2,6,6-tetramethyl-4-piperidinyl) sebecate (Tinuvin 770) in cured coating systems. External and internal standardization procedures using both isotopically labeled and nonisotopically labeled internal standards were attempted. Excellent accuracy ($\pm 10\%$), precision (RSD $< 5\%$), and detection limits (1 ng) were obtained for the isotopically labeled internal standardization procedure. Shortcomings of the external standardization and nonisotopically labeled procedures are discussed.**

In the brief period since its introduction in 1981 (*1*), fast atom bombardment mass spectrometry has become a widely used technique for the analysis of high molecular weight and/or thermally labile compounds (*2*). The fast atom bombardment ionization process appears to be identical in mechanism with the more well established secondary ion mass spectrometry (SIMS) ionization process (*3, 4*). The SIMS technique, however, is generally used to examine the surface of a solid sample directly, whereas FAB is generally used to desorb ions from a sample suspended in a liquid matrix like glycerol. For the analysis of organic molecular compounds, the liquid matrix effectively provides a renewable sample surface which greatly reduces primary beam surface damage problems. This permits an extended period of analysis and allows the use of higher primary particle currents which improves sensitivity.

It would also appear that the liquid matrix would greatly simplify quantitative analysis since internal standards can be easily incorporated into this medium. Relatively few studies have been made on the feasibility of quantitative FAB analysis. Gaskell et al. (*5*), Millington et al. (*6*), Murphy et al. (*7*), DeStefano et al. (*8*), and Ho et al. (*9*) have described quantitative FAB analysis procedures using isotopicaly labeled internal standards of steroid sulfates, acylcarnitines, blood platelet activating factor, surfactants, and dipalmitoylphosphatidylcholine, respectively. Teeter (*10*) has described an external standardization procedure for the quantitative FAB analysis of alkylbenzene and aliphatic sulfonate salts.

Recently in our laboratory the need arose to develop a quantification procedure to monitor the photostabilizer additive bis(2,2,6,6-tetramethyl-4-piperidinyl) sebecate (Tinuvin 770) (*11*) in cured paint as a function of weathering time. This paper describes a systematic study in which quantitation of this compound by FAB mass spectrometry was investigated using external, nonisotopically labeled internal, and isotopically labeled internal standardization procedures.

## EXPERIMENTAL SECTION

All FAB analyses were performed on a Vacuum Generators ZAB-2F mass spectrometer interfaced to an INCOS 2300 data system. The mass spectrometer was equipped with a Vacuum Generators modified Ion Tech, Ltd., B50 power supply and a B11 saddle field ion source as a primary atom gun. Xenon was used as a bombarding gas with an energy of 8 kV and at a neutral atom "current" of approximately 20–30 $\mu$A (1 mA power supply limiting current).

Industrial grade Tinuvin 770 obtained from Ciby-Geigy, Ltd., was triple-recrystallized from ethanol prior to use. The tetradeuterated analogue of Tinuvin 770, bis(2,2,6,6-tetramethyl-4-piperidinyl) 2,2,9,9-tetradeuteriosebecate, was synthesized by transesterification of the dimethyl ester of 2,2,9,9-tetradeuteriosebasic acid (Sigma Chemical Co.) with 4-hydroxy-2,2,6,6-tetramethylpiperidine (Aldrich Chemical Co.). Tricyclohexyl citrate (2-hydroxy-1,2,3-tricarboxylic acid tricyclohexyl ester) was used as supplied (Chem. Service, Inc.). Two coating systems were tested: a thermosetting acrylic melamine (*12*) and a hydroxy ester melamine (*13*). Glycerol used as a FAB matrix was diluted to 150 $\mu$g/$\mu$L in methanol to alleviate problems associated with handling small volumes of material.

Tinuvin 770 was extracted from a known weight (approximately 40 mg) of cured or uncured coating sample by soaking in 5.0 mL of methylene chloride for approximately 15 h. In internal standard experiments a known amount of tricyclohexyl citrate or deuterated Tinuvin 770 was also added to the mixture at the beginning of the extraction. The external standard FAB analysis was performed by placing 2.0 $\mu$L of extract or standard solution onto a 2 × 5 mm gold sample probe tip, allowing it to dry, then adding approximately 2 $\mu$L of glycerol/methanol solution (300 $\mu$g of glycerol). The sample and glycerol were mixed and most of the methanol was allowed to evaporate prior to insertion into the FAB source. The internal standard FAB analysis was accomplished in a similar manner except that only an approximate volume of sample and standard was initially added to the probe tip. Quantification was achieved by integrating the relevant ion

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