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Figure 3. Signal intensity vs. time for sample containing 114 pg of ^{99}Tc , neon fill gas

Either argon or neon seems to be satisfactory for filling the demountable lamp. However, neon gives a somewhat lower noise level and an absorption signal about 1.8 times greater than does an argon-filled lamp. Figure 3 is an example of the recorder output for a typical measurement with a neon-filled cathode containing 4.5 mg ^{99}Tc and a sample size of 114 pg ^{99}Tc . Calibration curves for both argon and neon were linear over the ranges studied, i.e., 0–914 pg ^{99}Tc for argon and 0–2900 pg ^{99}Tc for neon. The relationship found between peak height and quantity of technetium is given by the expressions $h = 0.095w$ for argon and $h = 0.151w$ for neon, where h is the peak height in milliabsorbance units and w is the weight of ^{99}Tc in picograms. For the case of argon, the milliabsorbance values were determined from an average of three peak height measurements at each of three different concentrations of ^{99}Tc . For neon, an average of three measurements at each of six different concentrations of ^{99}Tc was taken. The detection limit for technetium is about 60 pg when a neon-filled lamp is used. Detection limit is herein defined as the quantity of technetium which yields a peak-height value that is twice the standard deviation of the blank value.

Peak height values were determined for cuvette temper-

atures of approximately 2400, 2800, 3100, 3300, and 3400 °C during the 10-s atomization step. Increasing peak heights resulted from the higher temperatures, with incomplete vaporization of technetium occurring at the lowest temperature. A cuvette temperature of 3300 °C was chosen as a reasonable compromise between maximum peak height and long cuvette life.

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Low-Temperature Positive Secondary Ion Mass Spectrometry of Neat and Argon-Diluted Organic Solids

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Secondary ion mass spectrometry of neat solid propane, *n*-pentane, benzene, toluene, and of propane imbedded in an argon matrix were observed at temperatures varying from 10 to 110 K and show fragmentation patterns similar to those known from ordinary electron impact mass spectrometry. The effects of the nature and energy of the primary probe ion and of the sample temperature were investigated. The analytical potential of the method, e.g., for reactive species trapped in inert matrices, is noted.

In the course of work with heat-sensitive involatile organic

and biological materials and with highly reactive species isolated in inert matrices, it frequently appears desirable to complement other spectroscopic methods by mass spectral data. Since in these instances the species of interest cannot be easily transferred to the gas phase without change, standard mass spectrometry is of little direct use and methods such as field desorption (1) have been investigated. In recent years, a limited amount of exploratory work on organic solids using plasma desorption mass spectrometry (PDMS) (2, 3) and secondary ion mass spectrometry (SIMS) (4–18) has been performed in several laboratories and appears to show considerable promise.

In SIMS, a beam of primary ions or neutral atoms bombards a solid sample and etches its surface. The sputtered material is ejected as positive ions, negative ions, and neutrals. The secondary ions are collected and analyzed in a mass spectrometer. The method is well established as a tool for investigation of the surface of metals and semiconductors (4-7) and has also been used to study the absorption of hydrocarbons on such surfaces (19). We now report an investigation of the suitability of the SIMS technique for the characterization of organic samples held at cryogenic temperatures and the first SIMS measurement on an argon-matrix isolated species (20).

EXPERIMENTAL

The spectra were measured on a 3M Model 525 Ion Scattering and Secondary Ion Mass Spectrometer equipped with a 4096 channel Nicolet 1170 signal averager. The ion gun used in this instrument requires a stationary backfill of the sample chamber with the ion beam gas of about 6×10^{-5} Torr, and this limited our experiments to the use of helium and neon which do not condense on the cold sample plate at the temperatures we used (≥ 10 K for He, ≥ 35 K for Ne). The sample plate was made of oxygen-free high conductivity copper and was attached to the cold head of an Air Products Displex closed-cycle cryostat, whose temperature could be adjusted between ambient and 10 K. It was positioned in such a way that secondary ion mass spectrometry (SIMS) and ion scattering spectroscopy (ISS) could be performed simultaneously. In the 3M instrument, the secondary ions are not accelerated and those which reach the UTI Model 100C quadrupole mass analyzer attached at a 90° angle with respect to the ion gun give rise to the observed SIMS spectrum (a pre-filter removes neutrals and ions with kinetic energy higher than 20 eV). The rare gas ions scattered at 138° are analyzed by a cylindrical mirror analyzer and yield the ISS spectrum.

The vacuum system consisted of two sorption pumps and a Varian Vac-ion diode ion pump (500L/s). The liquid nitrogen cryopanel provided in the instrument was not used in the low-temperature experiments since the large cold surface of the closed-cycle cryostat already provided efficient cryopumping. After bakeout and before cryopumping and sample deposition, a background pressure on the order of 1×10^{-9} Torr was established. The remaining gas mixture contained primarily nitrogen and water, as established by remnant gas mass spectrometry.

The ion probe gases were (99.95% pure) ^3He and (99.98% pure) ^{20}Ne (Monsanto Research Corporation). The ion beam was defocused to about 2-mm diameter for the SIMS experiments (the largest of the three available beam sizes). The maximum available beam raster was used. The ion beam current was approximately $10 \mu\text{A}/\text{cm}^2$ but could not be measured exactly in these experiments, since the sample plate was grounded.

The organic samples used were of spectrograde quality except for propane, which was 99% pure (Union Carbide). Their vapors, pure or diluted with high purity (99.9995%) argon (Matheson Co.), were prepared in a separately pumped vacuum manifold, oil diffusion pumped to 1×10^{-6} Torr. About 1×10^{-4} mol were bled in over about 30 min through a calibrated leak valve which had an outlet about 0.5 cm above the cold sample plate, keeping the total pressure in the main chamber below 2×10^{-7} Torr whenever the vapor pressure of the sample at the temperature of the cold plate permitted. At low deposition temperatures (up to 35 K), where most of our work was performed, the sample formed an elongated spot near the center of the copper plate, but at the highest temperatures used, it covered most of the plate. At the lower temperatures, the pressure in the sample chamber was below 1×10^{-8} Torr after sample deposition and before admission of the ion beam gas, except in the experiments with argon. In the experiments performed at the highest temperatures used, the total pressure after sample deposition was of the order of 1×10^{-6} Torr. There is no doubt that in the experiments at 35 K and below, the measured signal originated in the surface of the organic solid and not in the small amount present in the gas phase, since the organic fragment ions gradually disappeared and were replaced by the ions of copper and its contaminants (Na, K) when the ion beam was deflected off the sample spot to a clean area of the plate.

Even at the higher temperatures, there is no evidence that any of the observed SIMS signal originated in the gas phase (see Discussion).

To obtain reliable SIMS data, the use of a low-energy electron floodgun was essential to overcome surface charging by continuous ion bombardment. The adjustment of the flooding current was done by trial and error until a stable maximum SIMS intensity was obtained. At lower floodgun currents and resulting positive charging of the sample surface, intensities of all peaks were lower, but their relative proportions remained nearly unchanged. However, higher than optimum floodgun currents were carefully avoided after it was found that they caused distortions in relative peak intensities, generally favoring fragments with lower m/e ratios (cf. Figure 1).

RESULTS

In the present study, ISS was used only to confirm the presence of carbon and argon on the appropriate section of the cold plate and to map out their spatial distribution by the rastering technique. ISS also gave useful information during depth profiling of the argon matrix isolated samples. However, our primary focus was on SIMS.

It was established rapidly that the spectra are well reproducible and that the fragmentation pattern is basically similar as in ordinary electron impact mass spectrometry. Noticeable differences occur in relative fragment ion intensities and are described further below for the four compounds investigated.

Effect of Experimental Variables on SIMS. The following observations were made for the four hydrocarbons.

(i) The spectra were independent of the sample temperature, and also the overall intensity did not vary significantly (the actual temperature range explored was a function of sample volatility, e.g., 10 to 110 K for *n*-pentane in 10° increments). At higher temperatures less electron floodgun current was required.

(ii) The spectra of the hydrocarbons were independent of the nature of the primary ions ($^3\text{He}^+$ or $^{20}\text{Ne}^+$). Only the relative abundances of the CH_2^+ and CH_3^+ fragments increased by a few percent when $^3\text{He}^+$ was used as probe ion in the spectra of propane and *n*-pentane.

(iii) The spectra were independent of the kinetic energy of the primary ions within the range 100 eV to 3 keV.

(iv) The spectra obtained at low probe ion energies (below 1 keV) were independent of time for several hours. At higher ion energies, especially above 2 keV and after prolonged ion bombardment at lower energies, gradual appearance of fragment ions of higher m/e ratios than the molecular ion was observed in the case of the two alkanes. In particular, we observed C_6 and C_7 fragments from *n*-pentane, and C_4 and C_5 fragments from propane. The abundance of these higher mass peaks remained low even after several hours (cf. Figure 2) and the intensity distribution of the other fragments was not affected. No signs of sample decay were observed for the two aromatics within our detection limits.

(v) The spectra of propane were of lower intensity but otherwise identical when it was diluted with argon up to the ratio 1:150 (Figure 3). In the diluted samples of propane, C_4 and C_5 fragments were not observed even after prolonged ion bombardment.

SIMS Fragmentation Patterns. The SIMS data for the solid samples were compared with those obtained for the same compounds in the gas phase using electron impact (50 eV) and the same UTI quadrupole mass analyzer. These latter spectra are similar to the electron impact spectra reported in the literature (21) but are not identical because of possible distortions due to the pre-filter and since the quadrupole mass analyzer favors the relative intensities of the lower mass fragments (the relative sensitivity curve for our analyzer is shown in Ref. 13). The comparison between the fragmentation

Figure 1. Neat *n*-pentane. Top: Electron impact mass spectrum obtained in the remnant gas analysis mode of the quadrupole mass spectrometer. Center: Positive SIMS (8 scans, 2-min scan time). The ^{20}Ne peak is due to traces of neon implanted in the matrix during a previous experiment with a $^{20}\text{Ne}^+$ beam. Bottom: Positive SIMS with electron floodgun current too low (A), optimum (B), and too high (C)

patterns obtained by SIMS and electron impact mass spectrometry revealed interesting differences in relative abundances of fragments.

(i) *n*-Pentane (Figure 1). Within each C_n group, the $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$ fragments are in general the most abundant. The former is the more abundant in electron impact mass spectrometry, but as could be expected (22), the

Figure 2. Positive SIMS of neat *n*-pentane after several hours of bombardment with 3-keV $^{20}\text{Ne}^+$ ions (higher mass region only, 32 2-min scans averaged)

Figure 3. Positive SIMS depth-profiling of a propane-argon matrix. Single 2-min scans. The A_2^+ peak has about 10% of the intensity of A^+ , all impurity peaks are even weaker

Figure 4. Positive SIMS of neat propane. A single 10-min scan. No peaks above noise level were observed at m/e values higher than those shown

latter is the more abundant in SIMS. Among the various C_n groups, the C_3 is most abundant in electron impact spectra (especially $m/e = 43$, $C_3H_7^+$), while the C_2 group is more intense in SIMS (especially $m/e = 27$, $C_2H_3^+$). The parent molecular ion peak, although weak, is easily observable in the

Figure 5. Positive SIMS. Top: neat benzene, bottom: neat toluene. Single 10-min scans

electron impact mass spectra, but is absent in SIMS. In SIMS, the highest m/e peak observed corresponds to the $(M-1)^+$ ion at $m/e = 71$.

(ii) *Propane* (Figure 4). The great similarity to the *n*-pentane spectrum is apparent. Again the strongest peak, C_2H_3^+ , is of the $\text{C}_n\text{H}_{2n-1}^+$ type. The C_2 fragments are the most abundant and no parent molecular ion fragment is observable. The highest m/e peak corresponds to the $(M-1)^+$ ion at $m/e = 43$.

(iii) *Benzene and Toluene* (Figure 5). Unlike the spectra of the alkanes, the spectra of both aromatics show the molecular ion peak, albeit in much weaker relative abundance than in the electron impact spectra. The most abundant fragment in SIMS is the C_3H_3^+ ion at $m/e = 39$ for both benzene and toluene, while in electron impact spectra it is the molecular ion for benzene and the $(M-1)^+$ ion for toluene. In both types of spectra, the CH_2^+ and CH_3^+ fragments are very weak or absent. The SIMS cracking patterns of both benzene and toluene show weak peaks of the $(M+1)^+$ ions in intensities far in excess of those expected for natural ^{13}C abundance.

(iv) *SIMS of Argon Matrix Isolated Propane* (Figure 3). Except for the presence of a strong A^+ ($m/e = 40$) peak, weaker A^{2+} ($m/e = 20$) and A_2^+ ($m/e = 80$) peaks, and for an overall decrease in intensity, SIMS of propane is the same for a neat solid and for molecules imbedded in a solid argon matrix. The highest dilution tried was 1:150 and the signal-to-noise ratio was still quite good even for a single scan, indicating strongly that even more dilute mixtures will be

amenable to SIMS investigations. The relative abundance of the argon ions and the organic ions shows an interesting time dependence at the beginning of ISS and SIMS experiments on a fresh argon matrix. At first, the relative abundance of the organic ions is very low compared with A^+ . As spectral scans are repeated, the abundance of the organic ions relative to A^+ ions gradually grows until it finally attains a plateau and shows no further change (Figure 3). This effect appears both in SIMS and in ISS. We assign these changes to a gradual removal of the topmost layers of the matrix by sputtering. It is reasonable that the layers which condensed last during the deposition should be enriched in the more volatile component.

DISCUSSION

Our main goal is to develop SIMS as a supplementary tool for identification of molecules isolated in inert matrices. To accomplish this, we need to show that such matrices are not destroyed by overheating, that the signal-to-noise ratios are adequate, and that the fragmentation patterns are insensitive to experimental conditions and are interpretable. Our secondary aim is to assess the usefulness of low-temperature SIMS for analysis of neat organic samples. Room-temperature measurements of this latter type have been reported both for selected low-molecular weight organic solids (13–18) and for several polymers (8–12), but little attention has been paid to the possible overheating and ion-molecule reactions in the neat solids. These dangers are minimized when very low primary ion current densities are used (static SIMS) (15, 16) but this then does not permit depth profiling which may be of considerable interest in analytical applications. The present results show that neither inadequate sensitivity nor sample destruction by overheating and secondary reactions are a problem with cooled samples under conditions of dynamic SIMS. Also, the cooled probe is advantageous for fundamental investigations of the fragmentation reactions since very simple hydrocarbon substrates can be used.

Our remaining concern has to do with the extent of ion fragmentation. If the fragmentation were excessive or strongly dependent on the experimental conditions, the value of the method as an analytical tool would be sharply decreased. Previous room-temperature SIMS data on organic solids coated on metals reported either relatively little fragmentation initially, but quite rapid decay of the sample with time (15, 16), or an extent of fragmentation which was higher than in ordinary electron impact mass spectra, but not prohibitive (13, 14, 17, 18). Our experience with the four molecules chosen for this study parallels the latter results: fragmentation is stronger than in electron impact mass spectra but is not prohibitive, and the fragment ion m/e values which emerge are those which have already proved to be useful in organic structure determination. The lack of sensitivity of the spectra to experimental conditions is encouraging. Since the instrument had no ion collection optics, its sensitivity was rather low, and, moreover, we cannot be sure that the relative abundances of the secondary ion detected are in any simple relation to the relative abundances of the secondary ions formed, and little can be said about mechanisms at this stage. Charge-transfer clearly is a strong candidate, particularly in view of the similarity of our relative fragment ion intensities to those reported in charge-transfer mass spectra (23), but it is interesting to note that we observe essentially no differences in spectra obtained with $^3\text{He}^+$ and with $^{20}\text{Ne}^+$, and that our spectrum of *n*-pentane is almost identical with the reported spectrum of polyethylene obtained using a neutral atom primary beam (12). Whether the ionization occurs on the surface or near the surface after ejection of the organic species into the vapor phase is presently not known. There is no doubt, however, that the observed fragments originate

from molecules which reside in the surface of the solid. This is particularly clear in the experiments at 35 K and below in view of the measured low pressure of the organic material in the gas phase ($<1 \times 10^{-8}$ Torr), of the parallel SIMS and ISS depth-profiling results, and of the experiments with an ion beam deflected to an uncoated area of the sample plate. The occurrence of higher mass fragments from the alkanes after extensive bombardment, in abundances independent of sample temperature (for pentane, up to 110 K), proves that even at the highest temperatures used little if any of the observed SIMS spectrum originates in the gas phase ($<1 \times 10^{-6}$ Torr). This conclusion is also in accordance with the lack of dependence on the nature of the primary ion, with the temperature-independence of the relative fragment ion abundances, and with the absence of any pronounced temperature dependence of the overall intensity.

It is clear that our experimental setup can be improved considerably, not only by extracting the secondary ions into the mass spectrometer, but also by insulating the cold sample plate electrically, permitting a measurement of the primary ion current and improving the floodgun control, and by using a differentially pumped ion gun which will allow the use of additional types of primary ions. With such improvements, it appears quite realistic to expect that even very dilute solid samples of organic materials will be amenable to SIMS investigations.

Important conclusions from this work for analytical use of SIMS on cooled organic solids are (i) while some bombardment damage to the sample undoubtedly occurs, it has negligible effect on the spectra observed under our conditions; (ii) the fragmentation pattern is insensitive to the type and kinetic energy of the probe ion and to the temperature of the sample; (iii) the extent of fragmentation is not prohibitive and the nature, but not relative abundances, of the fragment ions are identical to those known from electron impact mass spectrometry. Further work on various types of organic substrates is needed to establish the generality of these conclusions.

Possible applications of low-temperature SIMS are many, from analysis and depth-profiling of polymers and biological

materials to investigation of the course of metal atom aggregation or photochemical fragmentations in argon matrices and to investigation of fundamental aspects of ion-molecule reactions.

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Obsidian Characterization with Elemental Analysis by Proton Induced γ -Ray Emission

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The detection of γ rays which are emitted during proton irradiation of a sample provides a rapid method for the determination of element concentrations which is nondestructive and requires minimal sample preparation. With this method, standard deviations of 2 to 5% can be achieved in the determination of fluorine, sodium, and aluminum in obsidian. Results are given for 20 known sources of South-West Pacific obsidian and applied to the characterization of 700 artifacts discovered in this area. The advantages of the method make it superior to other techniques previously used for the study of obsidian.

Methods which have been used in the elemental analysis

of obsidian include optical spectroscopy (1), neutron activation analysis (2), X-ray fluorescence (3), and, more recently, proton-induced X-ray emission (4). The purpose of most analyses is to relate obsidian artifacts to known sources of raw material, through similarities in the concentrations of selected elements. Many different combinations of elements have been used for this purpose, the variations in single-element concentrations within one source being typically less than 10%. On the other hand, different sources show much larger changes in the concentration of some elements.

A large number of obsidian artifacts are available for study and it is important that the method of analysis be rapid, nondestructive and applicable to samples having a wide range of shapes and sizes with a minimum of preparation. These