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AN LC-MS USING ION IMPACT

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AN LC-MS USING ION IMPACT *

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The need for a liquid chromatograph-mass spectrometer interface which can efficiently handle nonvolatile and thermally unstable molecules is well recognized. Field desorption (FD) mass spectrometry is effective for the analysis of many such compounds but a direct interface between the chromatograph and the mass spectrometer has not been constructed due to the high voltages and precise mechanical alignment required. Existing commercial LC-MS interfaces use either: (a) a direct introduction of a small flow of the LC effluent directly into a heated chemical ionization (CI) source; or (b) deposition of the effluent on a moving ribbon with evaporation of the volatile mobile phase and progression through a series of vacuum locks, and volatilization or pyrolysis of the material in or adjacent to a conventional CI or electron impact (EI) ion source. These and related interfaces have been demonstrated to be effective for a wide range of compounds, but their application for the analysis of nonvolatile and thermally labile compounds is limited. Recently, it has been recognized that a variety of alternate ionization methods produce mass spectra which are remarkably similar to those obtained by FD. These techniques include "in-beam" chemical ionization on Teflon probes or special surfaces, secondary ion mass spectrometry (SIMS), Californium-252 plasma desorption, and laser desorption (LD).

We have recently constructed a moving ribbon LC-MS interface for operation with either SIMS or LD ionization methods and have begun to explore the ion impact approach. Figure 1 is a schematic illustration of the LC-MS interface and its integration into an analysis scheme which will use either SIMS or LD. The LC effluent is deposited on a slowly moving (5-30 cm/min) continuous ribbon (0.63 cm wide, 0.008 cm thick, 320 cm long). Ribbons of high purity (>99.999%) nickel, molybdenum, and platinum have acceptable mechanical properties and are readily spot welded to form the continuous ribbon. A unique feature of the interface is the inclusion of a 100-cm long evaporation region for the LC mobile phase before the first vacuum slit. This also allows the semipermanent storage of material. Evaporation is assisted by gentle heating (with the temperature of the ribbon maintained below the boiling point of the liquid) from strip heaters located just above and below the ribbon, a continuous flow of preheated argon, preheating of the liquid effluent, and the relatively slow speed of the ribbon. Preliminary tests show that one can readily evaporate to dryness a variety of liquids (hexane, water, etc.) deposited at 2 cm^3/min and at a ribbon speed of 20 cm/min prior to the first vacuum chamber. At the slowest speeds, some loss of chromatographic resolution appears unavoidable for less volatile solvents due to the finite period required for evaporation of the mobile phase and flow of the liquid on the ribbon surface. Three regions of differential pumping are employed prior to the high vacuum surface. The first two regions are pumped by Leybold-Heraeus S30A "hot pumps" (at 10 liter/sec) to limit the effects of condensable vapors during long-term pump operation, and the third by a 1500 liter/sec turbomolecular pump. The main drive wheel is also used to adjust ribbon tension and is motor driver through three universal joints; at no point does the sample surface of the ribbon contact another surface. Typical working pressures are approximately 20 torr, 0.5 torr, and 10^{-5} torr in the three differentially pumped regions. The pressure in high vacuum chamber ranges from 10^{-7} to 10^{-6} torr depending upon the required gas flow for the ion gun and mass spectrometer collision chamber.

Ions formed at the surface pass through a Bessel Box energy filter and are analyzed using either a single or a new double quadrupole mass spectrometer (Extranuclear Laboratories, Inc., Pittsburgh, PA) which incorporates a chamber for collision-induced dissociation (CID) fabricated of leaky dielectric material (approximating the middle quadrupole of triple quadrupole analyzers). The use of CID in conjunction with the LC-MS interface should greatly increase chemical specificity and the deconvolution of complex chromatograms. (The CID complements SIMS or LD ionization modes since these processes often produce spectra with intense molecular or quasi-molecular ion peaks and limited fragmentation.) The major difficulty of the SIMS ionization mode results from the high sensitivity for surface contaminants. This difficulty arises from the high sensitivity of the technique for surface species. We have demonstrated detection limits of <0.01 ngrams for an easily ionized material (arginine) while scanning (Figure 2). The large "background" is clearly associated with material on the ribbon; improved ribbon clearing techniques suggest the possibility of greatly enhanced detection limits.

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The moving ribbon interface has several potential advantages when used with SIMS or LD ionization modes, and CID in a double or triple quadrupole analyzer. First, the long evaporation region at atmospheric pressure easily allows complete evaporation of the LC mobile phase prior to the first vacuum slit. This reduces sample loss and degradation of chromatographic resolution with splashing and atomization of liquid. Second, the SIMS or LD ionization modes are highly localized processes; this allows the use of slower ribbon speeds than by "flash" heating for volatilization without loss of chromatographic resolution and removes ribbon temperature as an important variable in determining sensitivity. Third, the ribbon length and slow ribbon speed allow temporary storage of the separated materials for LC runs of 10-60 minutes, depending upon ribbon speed and required resolution, when the "cleanup" heaters and solvent clearer are "off." This is an important advantage since the SIMS or LD technique will consume only a minute amount of sample during the normal analysis. Figure 2 illustrates this behavior for arginine samples ranging from 1.0 ng/cm^2 to 500 mg/cm^2. The behavior for successive ribbon rotations (25 min/rotation) shows evidence of surface damage for larger samples. (The "noise" is periodic in nature and representative of contamination.) Thus, temporary storage allows selected portions of the separated materials stored on the ribbon to be reanalyzed after completion of the separation and initial analysis. Selected ribbon locations can be analyzed for extended periods to increase the signal/noise ratio and detection limits. More important, however, the subsequent analysis allows one to completely utilize the CID capability of a double quadrupole mass spectrometer, which can only be applied during the initial separation to a limited extent due to mass spectrometer scan speed limitations. Thus, the SIMS ionization mode uniquely complements the storage capability of the interface; we are continuing to explore these analytical techniques using both the SIMS and LD ionization modes.

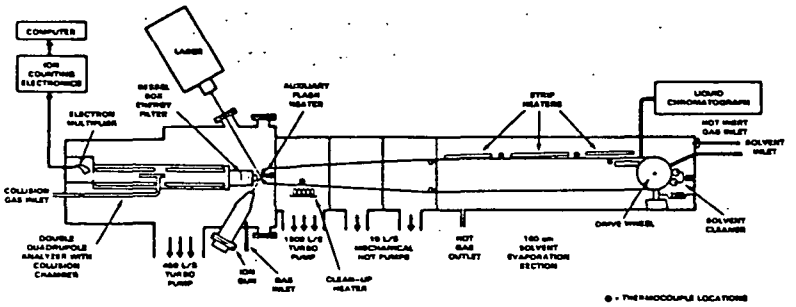

FIG. 1. Schematic illustration of the LC-MS using a moving ribbon interface, ionization by SIMS or LD, and analysis using a double quadrupole mass spectrometer.

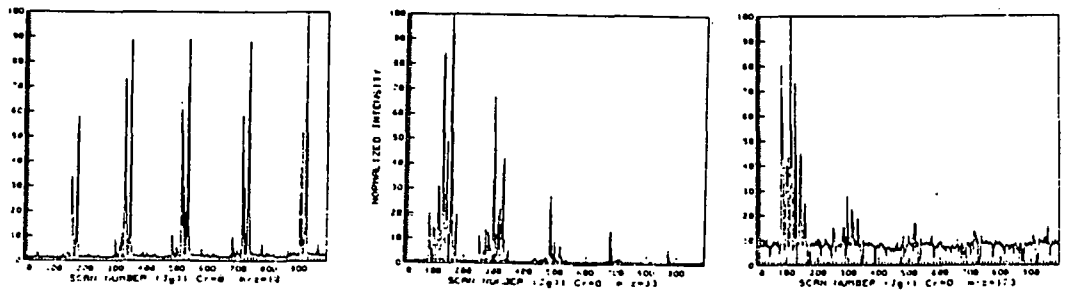

FIG. 2. Normalized intensities for ions at m/z 173, 33, and 18 for high current Ar^+ ion bombardment of seven samples of arginine in water deposited for one minute intervals alternated with blanks. Concentrations range from the equivalent of 1.0 nanogram/cm^2 to 1.0 milligram/cm^2 in decade intervals. Note the suppression of ionization indicated for m/z 173 for the most concentrated sample and the evidence of surface damage leading to a decrease of the m/z 173 and 33 ion counts and an increase in m/z 18 counts.