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Thin films preparation by the electrospray method in heavy ion induced desorption experiments

THIN FILMS PREPARATION BY THE ELECTROSPRAY METHOD IN HEAVY
ION INDUCED DESORPTION EXPERIMENTS

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ABSTRACT

Some details of the experimental procedure used to prepare thin films of organic compounds by the electrospray method are reported.

1.-INTRODUCTION

252
Cf-plasma desorption mass spectrometry (Cf-PDMS)
(1)
was introduced in 1974 as a powerful technique for molecular weight determination and fragmentation studies of biomolecules. It was observed that molecular ions and fragments could be desorbed from the sample surface by high-energy (MeV/A) heavy ions, as fission fragments from a 252 Cf source, or collimated beams extracted from accelerators. Secondary ions could be mass-analyzed by measuring their time-of-flight along a fixed path after being accelerated by a voltage difference.

The technique is now widely used in physics, chemistry and medicine with different aims, including molecular weight determination, fragmentation studies, investigation of the desorption mechanism, surface analysis, ... (2)

The sample preparation technique is an important step of the method, since normally this involves the study of involatile, thermally labile molecules. Different techniques have been employed to produce suitable thin films for PDMS studies, including vacuum evaporation, solution evaporation, electrodeposition, spin-casting and the electrospray method (3,4,5). The latter method has proved to be widely applicable to a large range of inorganic and organic solute species.

In this note we report some details of the experimental procedure which was carried out to prepare thin films of organic compounds by the electrospray method for planned PDMS experiments.

Both a home made electrospray unit and a commercially available apparatus were employed for these tests. (6)

Most of the reported results will refer however to the latter system.

2.-THE ELECTROSPRAY METHOD

In the electrospray method a glass tube with a capillary at the end is filled with a solution of the compound to be sprayed. The capillary is placed at a short distance from a collector foil and a voltage difference of a few KV is applied between the foil and an electrode immersed into the solution (see fig. 1).

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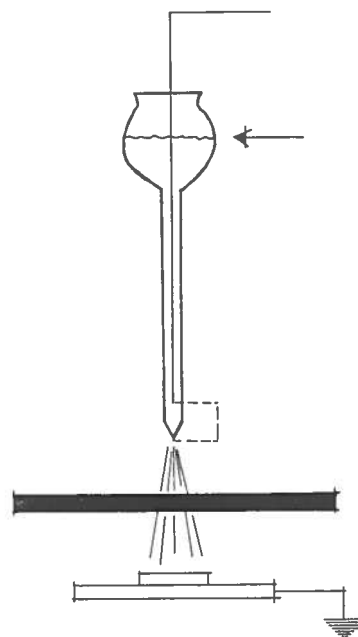
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Fig.1: Schematic set-up of the electrospray apparatus.



When the voltage difference is set, the liquid is forced out of the capillary in small droplets forming a cone. Since the solvent has a high volatility, only the solute particles can reach the foil, giving a thin film of the compound deposited on the backing.

The method has quite a long history in nuclear and applied physics (7-9) and it is proved very reliable to prepare sample film for desorption studies of organic compounds (5).

The conditions to obtain good spraying were found to be dependent upon many parameters, including the choice of the solvent, the applied voltage and the relative geometry of electrode and collector foil. Brunnix and Rudstam have reported a set of different results about the influence of these parameters (4).

3.-EXPERIMENTAL SET-UP AND PROCEDURE

Most of the tests reported here were made by using a commercially available apparatus ⁽⁶⁾.

The unit has a glass capillary with an electrode wire inserted; the other electrode is the sample backing made of a thin Al or aluminised plastic foil mounted between two brass rings. A rotating disc can hold different sample foils. Discrete rotation of the disc makes it possible the positioning of each foil under the capillary; the sample holder may also be X- and Y- positioned through adjusting knobs. A voltage V_e may be applied between the electrode wire and the sample foil. A focussing ring is also provided which can be maintained at a voltage V_F and distance from the collector foil intermediate with respect to the capillary. The capillary-sample and focussing ring-sample distances can be continuously adjusted.

A protective glass guard with a dark side at the back is placed around the system to minimize dust contamination and air flow during the electrospray.

A high intensity lamp was also used to illuminate the spray region in order to optimize spray conditions.

The procedure requires some experience to get good results. Some caution is to be used to clean all parts of the spray system. Before each test the capillary was rinsed several times with the pure solvent. Both capillary and electrode wire were cleaned after being used by leaving them in the solvent only for up 24 hours. A good advise is to use a capillary for each different solvent in order to prevent

contamination. Another critical factor is the surface of the backing foil, which must not be contaminated by dust, finger-prints,... to avoid non uniform deposition of the solute.

The spray conditions (voltages V_A and V_F , distances,...) need to be optimized by electrospray of the solvent only, before introducing the solution in the capillary.

The solvent is introduced into the capillary and the end of the electrode wire is adjusted around 0.5 mm above the capillary outlet. Non-correct positioning of the wire may result in solvent dropping, in which case good spray cannot be obtained.

The distance between capillary and foil depends on the sample area to be covered; it usually varies around a few (2-4) cm. Two sample backings are put in the sample holder: the first one is used to preliminarily adjust the spray with the solvent, while the next one is used for the sample. By filling the capillary with pure solvent and carefully applying the voltage V_A to the electrode wire (6-8 KV) a conical jet of spray exiting from the capillary may be seen under a high intensity illumination.

Only the above part of the spray cone is seen during this phase, since the solvent is fastly volatilized at the exit from the capillary. Better spray conditions may be found by applying a voltage V_F to the focussing ring at a distance approximately equal to half the capillary-sample distance.

By adjusting the voltage V_A , V_F and the corresponding distances as well as the X - Y position of the sample, a stable, uniform and well-centered spray cone may be obtained.

Once the best conditions are reached, and the capillary is empty, the chosen quantity of solution can be introduced into the capillary by a pipette of insulating material. Further small adjustments of the spray conditions may be obtained by observing the conical jet and the area which is being covered on the foil. At this point the clean foil is put under the capillary by a rotation of the disc and the spray is continued until the capillary is empty.

4.-RESULTS AND DISCUSSION

We found that many correlated parameters may influence the spray conditions. By varying the capillary - sample distance D different results may be obtained concerning the area covered by the sample, the electropray rate and the value of the acceleration voltage V_A needed to get a stable spray. The electropray rate is also influenced by the exact position of the electrode wire inside the capillary. Optimal value of these parameters can only be selected after several trials depending on the solvent and sample. As an example we report in fig. 2 the range of acceleration voltage V_A for which it was possible to obtain a stable spray with pure solvent (Methanol, CH_3OH) as a function of the distance D . Outside this range the spray was characterized by a rather irregular flow and not well focussed.

252

An important factor in the CF-PDMS technique is the fraction of surface covered by the sample since it gives the yield of molecular ions. This fraction depends also on the concentration of the solution. To have some idea of the quality of the electropray deposit, we made a few electron

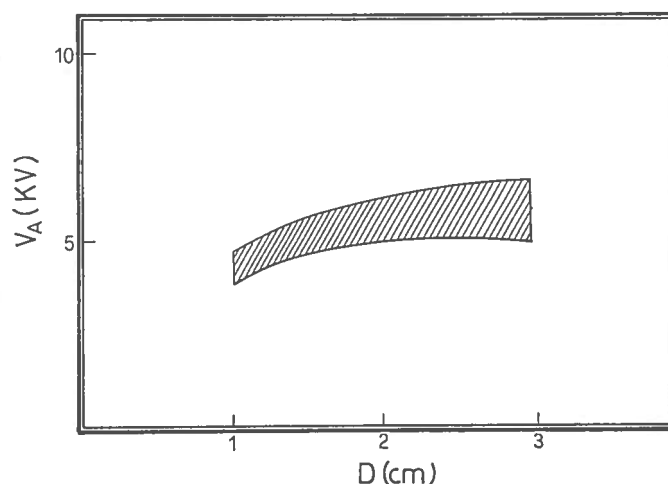


Fig.2: Range of acceleration voltage V_A as a function of the capillary-sample distance D . Hatched area covers the range for which a stable spray could be obtained, by using Methanol as pure solvent. Focussing voltage V_F was set to zero. Outside the hatched area the spray was irregular and not well focussed.

micrographs of Valine ($C_6H_{11}O_2N$, mol. weight 117) prepared from solution of $1\mu\text{g} / 1\mu\text{L}$ in Methanol on a aluminised polypropilene 1.5μ foil. Spray conditions were $V_A = 6 \text{ KV}$, $V_F = 2.5 \text{ KV}$, $D = 2,5 \text{ cm}$.

Figs 3 and 4 show the electron micrographs which refers to a total amount of solution of $10\mu\text{L}$ and $20\mu\text{L}$ respectively. The electrospray method produce charged droplets of μm size that evaporate during the path from the capillary to the foil. Only the solute residue from each droplet is deposited on the surface. The size of the residue from these droplets was found to be dependent on the concentration of the solution.

(5)



Fig.3: Electron micrograph of Valine deposit obtained by the electrospray method. Concentration of the solution was $1\mu\text{g}/1\mu\text{L}$ in Methanol. Total amount of solution sprayed: $10\mu\text{L}$.



Fig.4: Same as fig.3, but the total amount of solution was $20\mu\text{L}$.

In conclusion, the electrospray method has proved to be a suitable technique for PDMS studies. Its advantages include :

- i) the possibility to spray very small amount of the sample in a uniform way;
- ii) the applicability to a wide range of inorganic as well as organic species with different solvents;
- iii) the use of the method even for thermally labile

molecules; iv) the reasonable control and reproducibility in film preparation ; v) the high transfer efficiency.

Even if the method could be used in a routinely way, some experience and a carefully inspection of many parameters is however required in order to get good results.

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REFERENCES

- (1) D.F Torgerson, R. P. Skowronsky and R.D. MacFarlane, Biochem. Biophys. Res. Commun. 60(1974)616.
 - (2) R.D. MacFarlane and B. Sundquist, Mass Spectrom. Reviews 4(1985)421 and references therein.
 - (3) G.Save, P.Hakansson, B.U.R.Sundqvist and U.Jonsson, Nucl.Instr. and Meth. B26(1987)571.
 - (4) E.Brunnix and G.Rudstam, Nucl.Instr. Meth. 13(1961)131.
 - (5) C.J.Mc Neal, R.D.MacFarlane and E.L.Thurston, Anal.Chem. 51(1979)2036.
 - (6) BIO-ION Nordic AB, Uppsala, Sweden.
 - (7) D.Carswell and J.Milsted, J.Nucl. En. 4(1957)51.
 - (8) J.Zeleny, Phys. Rev. 10(1917)1.
 - (9) M.A.Nawab and S.G.Mason, J.Colloid. Sci. 13(1958)79.
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