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Peer-reviewed version available at Condens. Matter 2018, 3, 21; doi:10.3390/condmat3030021

Article

Microdrop Deposition Technique: Preparation and Characterization of Diluted Suspended Particulate Samples

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Abstract: The analysis of particulate matter (PM) in dilute solutions is an important target for environmental, geochemical and biochemical researches. Here we show how the microdrop technology may allow to control, through the evaporation of small droplets, the deposition of insoluble materials dispersed in a solution on a well-defined area with a specific spatial pattern. Using this technology the superficial density of the deposited solute can be accurately controlled. In particular, it becomes possible to deposit an extremely reduced amount of insoluble material -in the order of few μg- on a confined area, thus allowing a relatively high superficial density to be reached within a limited time. In this work we quantitatively compare the microdrop technique for the preparation of particulate matter samples with the classical filtering technique. After having been optimized, the microdrop technique allows to obtain a more homogeneous deposition and limit sample consumption of a factor ~25. This method is potentially suitable for many novel applications in different scientific fields.

Keywords: ultra-dilution; droplets; water; evaporation; X-ray fluorescence

1. Introduction

When dealing with complex samples, one of the main bottlenecks from the practical point of view is their preparation. A suitable sample preparation method should allow saving time during data acquisition, enhancing the S/N ratio, improving the detection limits, etc. Considering particulate matter (PM) analysis of solutions, the most common preparation technique is filtration: it is easy, reliable and fast, but at the same time it presents some drawbacks. Indeed, it requires a considerable sample consumption and PM whose size is smaller than the one of the filtration pores, are not retained on the filter. To avoid this point, the original solution could be deposited on a membrane presenting a quite large surface (about 1 cm^2). In this case a critical issue is the low superficial density of the PM deposited on top of it.

The evaporation process, based on the deposition of micro-droplets, may overcome both issues. Indeed, the microdrop technique consists in the deposition of PM in association to liquid drops presenting a diameter between 70 and 200 μm. After the evaporation of the solvent, the PM depositional pattern resembles the one of the original droplets. The main disadvantages of this method are the inhomogeneity of the deposition and the long time required for the evaporation of the solvent. In fact, the evaporation of large drops (few mm of diameter) can last several hours. At

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normal conditions of temperature and humidity, full evaporation of drops of water can require more than 10 hours per ml and the density fluctuation of the deposited material is up to 80% as a consequence of the so called coffee-stain effect [2]. To optimize the process, we deposit micro-droplets and control the deposition area with motorized translational stages. To this purpose a study of the evaporation dynamics is necessary to investigate the uniformity of deposition and to evaluate the evaporation rate of micro-droplets presenting different sizes. When dealing with densely packed deposition patterns our results show that is necessary to consider the interaction between different evaporating droplets.

The evaporation of a drop on a surface can be described with two different models: the evaporation with a "constant contact area" and that with a "constant contact angle" [1] (see figure 1).

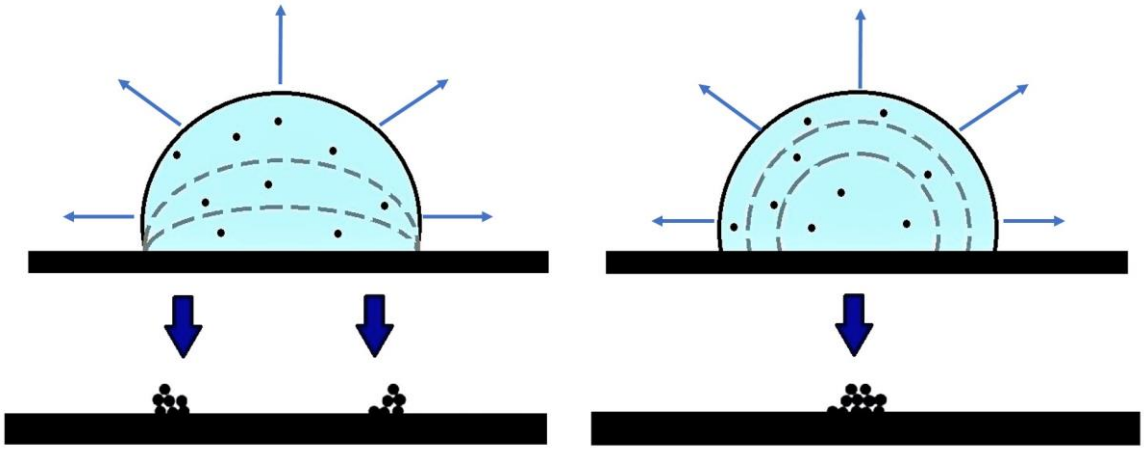

Figure 1: Deposition and evaporation processes for two different models: "constant contact area" (left) and "constant contact angle" (right). The main difference is represented by the shape of materials deposited on the substrate: pinned at the edge for the "constant contact area" model (bottom left) and concentrated in the center for the "constant contact area" model.

In the first case, the evaporation takes place maintaining a constant contact area between the liquid drop and the surface. The shape of the drop remains almost "spherical" [1], but the contact angle decreases. In accordance to the second model, the contact angle of the edge of the drop is constant during the evaporation [2], thus the shape of the drop remains "spherical" but the contact area between liquid and surface continuously decreases. The "constant contact area model" is suitable when a strong interaction between the liquid and the substrate takes place, as when considering water and a hydrophilic surface [3,4]. On the opposite, the second model is more appropriate when the drop-substrate interactions are weak, as in the case of water on a hydrophobic substrate.

In this contribution we will describe the optimization process of an experimental setup based on the evaporation of water micro-droplets in accordance to the constant angle model. The uniformity of the deposition will be determined and the results will be compared to the ones obtained through a classical filtration technique.

2. Experimental

Using a micro-dispenser, micro-sized droplets can be deposited controlling the spatial distribution of drops, their size and the deposition rate. The Microdrop technology [5] allows spreading extremely small amounts of a liquid solution. Moreover, thanks to dedicated devices, it is possible to deposit single droplets whose volume is in the sub-nanoliter range. Such small droplets present an interaction with the substrate, which can be considered negligible. A micro-dispenser is composed of a head with a nozzle and a pumping chamber working with the same piezoelectric technology used for inkjet printers. The head is controlled by a driver, i.e., a pulse generator, which controls the piezoelectric actuator and sends pulses to the head. The device we used is the MD-K-130 (© Microdrop Technologies), with an inner nozzle diameter of 70 μm that produces droplets with a minimum

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volume of 180 pl and a tunable drop rate from 1 to 2000 Hz. To prepare a sample with a specific microdrop pattern, it is necessary to control the number of drops on the substrate, releasing each of them at a well-defined and repeatable distance. In our experimental setup, to generate the pattern, the head is maintained fixed while the substrate translates under the stream of droplets released by the head. The motion of the substrate is realized with two precision PI Micos Translational Stage VT-80 stages, assembled perpendicularly with respect to each other. This setting allows positioning the substrate with a nominal accuracy of 1 μm per axis. The desired spatial patterns are obtained controlling the two translation stages with a LabView© based code and properly setting the Microdrop dispenser [6].

The characterization of the evaporation time and of the drop pattern was made with an optical microscope coupled to a video camera. The evaluation of the PM deposition uniformity has been performed using the x-ray fluorescence technique on the B18 beamline at the *Diamond Light Source* facility [7], using a monochromatic x-ray beam at 8 keV and with a focus of 100x100 μm².

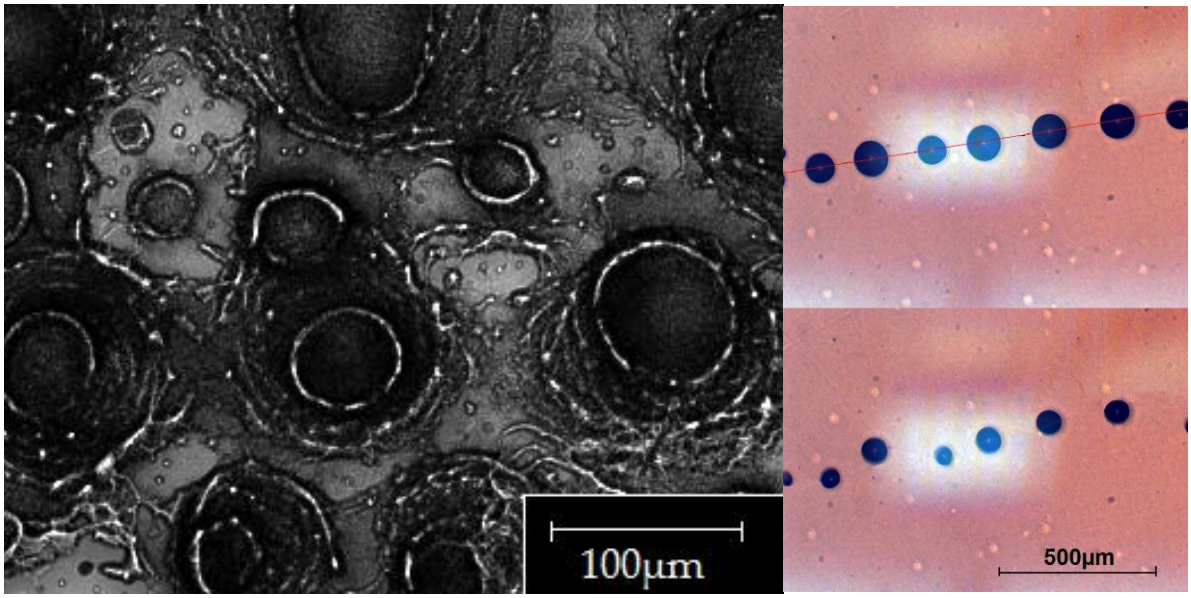

Figure 2: Optical microscope image taken at 20x magnification of a microdrop deposition of an ink solution (left). On the right two microscope images taken at 5x magnification of an evaporating line of droplets: one at the beginning of the evaporation (top right) and the second after 10 seconds (bottom right).

The evaluation of the evaporation was carried out measuring the diameter and height of droplets as a function of time using the optical microscope and the camera. We measured the parameters of the single droplets and of groups of droplets to evaluate the evaporation rate as a function of the size and of the distance between several droplets. We then identified the minimum deposited area achievable with the evaporation of small droplets, in the shortest time. To optimize the deposition process, all images and experimental parameters were analysed and used to write an approximate model.

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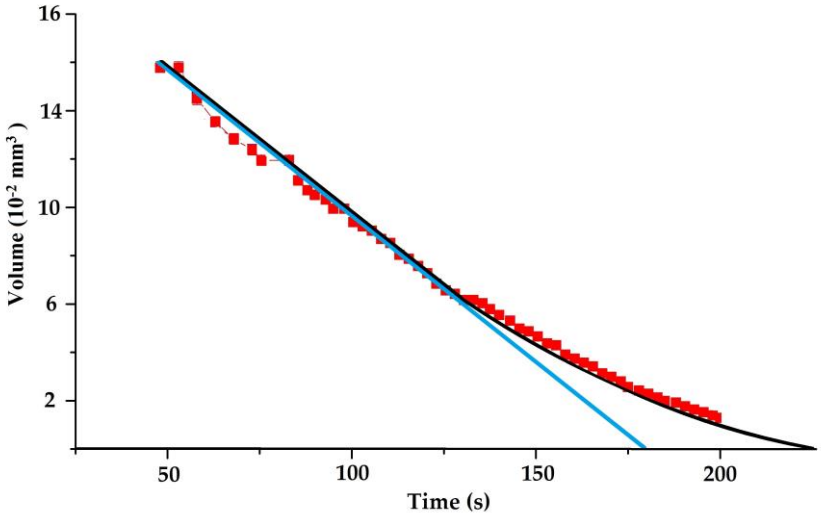

Figure 3: Comparison among the droplet mass behavior for the evaporation at "constant contact area" (blue line), at "constant contact angle" (black line) and experimental data (red squares) of a droplet of a bi-distilled water solution with an initial diameter of 1 mm, at room temperature.

3. Results

The analysis of the images of the droplets (see Fig. 2) and of the measured parameters, clearly points out that using a low concentration solution and a hydrophobic substrate as *Kapton*, the evaporation occurs in accordance to the "constant angle" model, well described by the theoretical model introduced by Picknett and Bexon in 1977 [1]. The result is confirmed in Figure 3, where our data are compared to the "constant angle" and "constant contact area" models. The deposition rate, i.e., the volume of the liquid deposited vs. time, was optimized considering the velocity of the stages and the spatial pattern parameters of the deposited droplets. Indeed, a fundamental parameter that drives the evaporation, is the saturation of the atmosphere surrounding the droplets selves, which is directly related to the mutual position of the droplets. Different droplet sizes and different distances between successive droplets were considered to this aim. Detailed results presented in Figure 4 point out that the highest evaporation rate at 20° C (~ 0.7 ml/h cm²) is obtained setting the droplet diameter at 240 μm and the distance between two consecutive droplets at 170 μm.

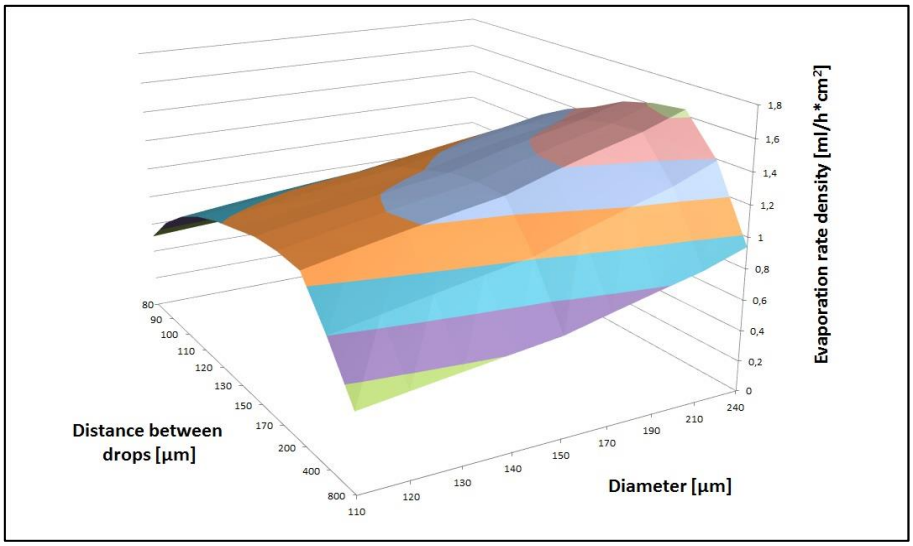

Figure 4: Graph of the volume evaporated per hour and of the area vs. the drop diameter and the distance (among two consecutive drops) at 20° C. To calculate the volume evaporated vs. time and the area we considered also the speed and the delays of the motorized stages.

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Closer drops would determine a higher relative humidity in the air layers which surround the drops selves, slowing the evaporation process. On the opposite placing drops at larger distance would limit the amount of deposited liquid with respect to the considered area, reducing the integrated efficiency of the process.

To further increase the evaporation rate, experiments conducted heating the substrate were also carried out. As expected, increasing the temperature evaporation rate increase following a power law with exponential value of the temperature of ~2,5. For example at 80° C the evaporation rate increases about 30 times [6]. However, it is worth noting that increasing temperature could not be always feasible, since increasing the temperatures the chemical stability of the samples may be affected. To avoid the problem, thermal radiation focused on droplets may be considered. Selecting specific wavelengths or frequencies it would be possible to selectively increase the temperature of the solvent and not the one of the PM contained in the solution. Another parameter, which could be modified to fasten the deposition, is the speed of the two motorized stages. Our experiments were all conducted at the maximum allowed speed (i.e., 13 $mm \cdot s^{-1}$), but faster motorized stages exist that allow to cover the same area with a shorter time.

To better understand the deposition pattern of the PM contained in a liquid solution deposited with a Microdrop dispenser, we prepared a suspension consisting in high purity water (MilliQ technology) and a given amount (50 μg/ml) of a reference material: the NIST standard 2709a. The latter is a well-known soil reference material with a well characterized composition [8] and grain size distribution. To avoid the clog of the Microdrop nozzle we selected a reference material whose particles didn't exceed 30 μm, i.e., about the half of the aperture of the nozzle orifice, as showed in Figure 5.

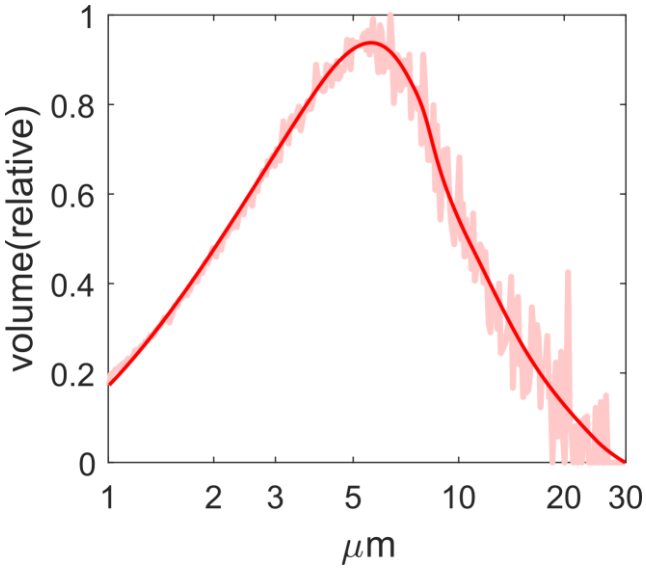

Figure 5: The particle size distribution of the NIST standard reference soil material 2709a. Data were obtained through the Coulter counter technique. Details can be found in Ref. [10].

Since the standard contains Fe, it was possible to use the X-ray fluorescence (XRF) technique to investigate its spatial distribution after deposition. In Figure 6 we compare two XRF profiles collected on two deposited samples, measured along a straight line. The red curve is the profile relative to the deposition of a single large drop of ~1 ml volume of the NIST solution. The black curve refers to a deposition obtained with the microdrop. The same total volume and the same solution were considered. The two profiles show significant differences and it is remarkable the homogeneous deposition obtained with the latter technique, despite the reduced amount of solution. Indeed, the large drop shows density fluctuations from 50% to 80% of the fluorescence intensity, in particular at the edge due to the coffee-stain effect [2]. At variance the variability observed along the microdrop profile is around 10 % and the deposited soil is uniformly distributed.

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Figure 6 clearly shows that the homogeneity and the overall quality of the samples prepared with the microdrop increase. The only disadvantage of this method is the deposition time. Indeed, as it can be inferred from Figure 4, the optimal configuration of this micro-deposition allows to deposit and to evaporate liquid samples with a rate of less than 1 mL per hour. A simple and alternative way to reduce the deposition time can be obtained combining the microdrop deposition with a simultaneous filtering technique. In this way the droplet is deposited onto a wettable filter and the liquid is pumped out by a vacuum pump.

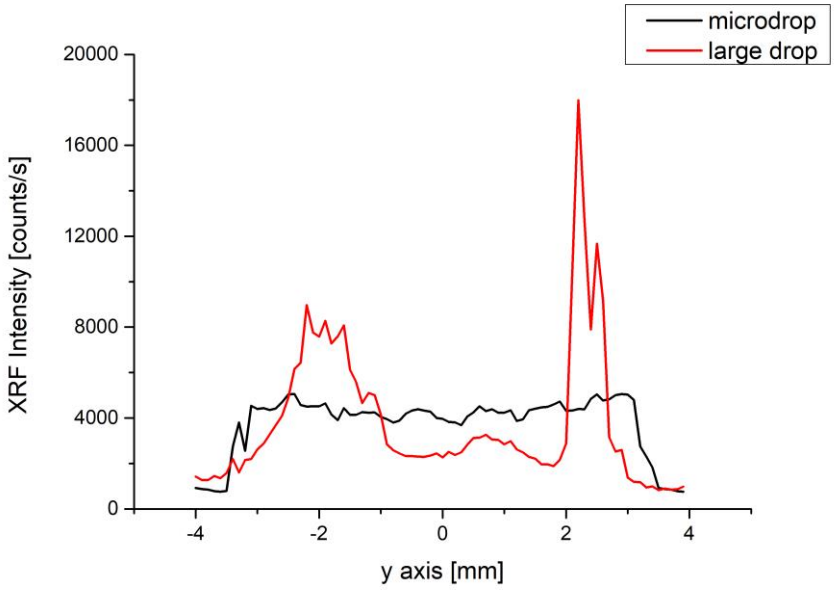

Figure 6: Comparison of two representative X-Ray Fluorescence profiles at the Fe K-edge: microdrop (black) and a single large drop (red) deposition of a NIST solution using ~1 ml volume.

In Figure 7 (left) the 2x5 mm^2 image shows a portion of the original 4x4 mm^2 microdrop deposition area of 1 ml NIST solution (50 μg/ml concentration) on a polycarbonate Nucleopore© membrane filter (pore size 0.45 μm and filter area diameter ~ 20 mm), which is a hydrophilic substrate. The color map was obtained collecting the XRF signal at the Fe K-edge. Colors highlight an area of approximately 2x3 mm^2 where a controlled distribution is achieved. The internal variability is probably also related to the spatial pattern of the pores characterizing the filtration membrane.

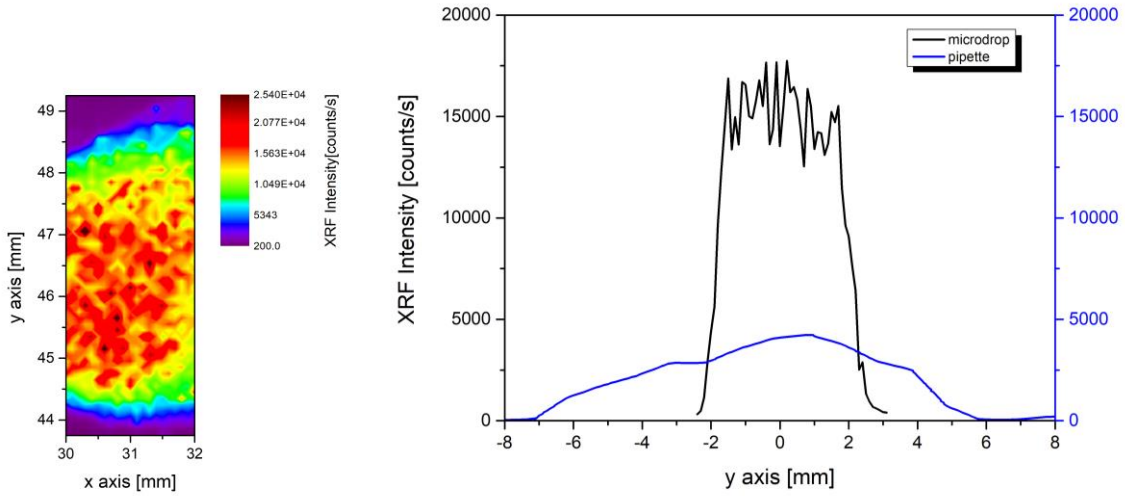

Figure 7: Image of the X-Ray Fluorescence at the Fe K-edge of the microdrop deposition area on the filter (left); comparison of two XRF profiles (right): the microdrop deposition (black) and the pipette deposition (blue) both achieved with a simultaneous vacuum filtration technique.

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In Figure 7 (right) one microdrop deposition profile of the image on the left is compared with an analogous profile of the deposition of the same solution using a micro-pipette on the same type of filter. From the analysis of the data, we may point out that using the microdrop deposition ~80% of the material is distributed quite homogeneously (with a fluorescence intensity fluctuation of ~15%) inside an area of ~8 mm^2. Using the pipette deposition the same amount of material is deposited within an area six times larger (~50 mm^2).

Conclusions

The microdrop technology is suitable to prepare homogeneous deposition of particulate and granular matter samples. In order to establish a reliable procedure, reducing also the deposition time, it is necessary to measure accurately the evaporation rate of the pattern depositions. We show here how to optimize such parameters, increasing the S/N ratio and the deposition homogeneity reducing at the same time the sample consumption. In terms of deposition uniformity, the microdrop technique allows reducing of a factor ~5 the heterogeneity with respect to a classical filtration method. At the same time the S/N ratio may improve ~4 times. These features make this technique effective and competitive with respect to many and diverse applications. Among the many, we cite the characterization of aerosols for pollution monitoring purposes, studies of metallic contaminants in polluted water or the investigation of biological diluted materials at ultra-trace concentrations. Besides homogeneity, another important feature of the method proposed here, is the possibility to concentrate in a very reduced area the material contained in an extremely diluted solution or suspension. This makes it possible to consider impurities whose concentrations span from few ppb to hundreds ppm. As an example, the method is suited for the characterization of the inorganic insoluble particulate matter contained in ice core samples for paleoclimatic reconstructions. Ice core dust samples prepared with a microdrop device could be successfully used for both X-rays absorption and X-ray Fluorescence measurements [9,11] and under particular experimental condition also for XRD experiments [12].

Acknowledgments: This research is a collaboration among *INFN-Laboratori Nazionali di Frascati*, *Milano Bicocca University* and the *Diamond Light Source* facility. The development of the microdrop instrumentation is a project managed by A. Marcelli with the support of *DARST - Department of the Presidenza del Consiglio dei Ministri*, which is gratefully acknowledged. Part of the preparation was done in the *EuroCold* Laboratory at University of Milano Bicocca, founded by Italian National Science Foundation NextData Project. Part of this research was developed at *Diamond*, the UK national synchrotron radiation facility. One of us (S.M.) acknowledges the *Roma Tre University* for financial support during his stage at *Diamond*.

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