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Spray-loading: A cryogenic deposition method for diamond anvil cell

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An efficient loading technique has been developed for flammable, toxic, or explosive gases which can be condensed at liquid nitrogen temperature and ambient pressure in membrane diamond anvil cells (DACs). This cryogenic technique consists in a deposition of small quantities of the desired gas directly into the sample chamber. The deposition is performed using a capillary that reaches the space between the diamond anvils. The DAC is kept under inert gas overpressure during the whole process, in order to avoid contamination from atmospheric O₂, CO₂, and H₂O. This technique provides significant advantages over standard *cryo-loading* and *gas-loading* when the condensation of dangerous samples at liquid nitrogen temperature raises safety concerns because it allows dealing with minimum quantities of condensed gases. The whole procedure is particularly fast and efficient. The “spray-loading” has been successfully used in our laboratory to load several samples including acetylene, ammonia, ethylene, and carbon dioxide/water or red phosphorus/NH₃ mixtures. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5011286>

I. INTRODUCTION

Sample preparation in a Diamond Anvil Cell (DAC) represents a crucial part of high pressure experiments, and the loading procedures are often the most challenging tasks. Typically, solid and liquid samples can be directly loaded between the anvils, inside the gasket sample chamber, and the cell can be closed by applying external pressure. The entire operation can be executed using a microscope to visually inspect the sample, and the procedure can be conducted in a safe environment provided, for instance, by a glove-box. The loading of gaseous samples is instead much more complicated, and the good method to achieve it strictly depends on the thermodynamic and chemical properties of the gas itself. Generally, the idea behind the loading of gases is to condense them at a low temperature or at high pressure. In any case, it is mandatory to put enough matter between the anvils for preventing the closure of the gasket hole when external pressure is applied. The two main techniques to achieve these objectives are named *cryo-loading* (low temperature and low pressure) and *gas-loading* (room temperature and high pressure). Both these techniques require dealing with large quantities of condensed gases. *Cryo-loading* is used for gases with the boiling point and melting point, respectively, above and below 77 K,¹ while *gas-loading* is employed for gases with the boiling point lower than 77 K, where the production of a sufficiently dense fluid to fill the sample chamber is needed.² These efficient methods are widely used, but the main disadvantage emerges when dealing with

dangerous chemical species, such as explosive (i.e., C₂H₂), toxic, or corrosive (i.e., NH₃) gases. In fact, handling large amounts of these kinds of chemicals could be very dangerous for the operators as well as for the instrumental equipments. Moreover, *cryo-loading* is typically performed using liquid nitrogen baths, where the temperature is fixed to 77 K, or commercially available cryogenic baths, which typically allow controlling temperature only down to 223 K. If the gaseous sample solidifies in this temperature range, its solidification inside the cryogenic vessel may raise serious safety issues due to the blocking of in/out tubes. Furthermore, the solidification could prevent the mechanical closure of the cell. Finally, for the loading of mixtures of species having very different melting and boiling points, both these standard techniques are not suitable.

To overcome these limitations, and specifically for loading acetylene and ammonia, we have developed a novel technique that allows us to work with really small quantities of condensed gas, avoiding risks related to explosive, corrosive, or toxic chemical species, and to perform depositions of mixtures whose components are characterized by very different melting points. This technique is based on a cryogenic procedure aimed at performing an *in situ* deposition of the desired amount of condensed gas, by means of a capillary directly reaching the sample chamber of the DAC, delimited by the anvils and the gasket hole, and has thus been called *spray-loading*. The experimental apparatus is simple and easy-to-build, and we realized it with very low budget, exploiting the resources and the expertise of the European Laboratory for Non-Linear Spectroscopy (LENS) Mechanical Workshop.

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II. APPARATUS AND METHOD

The design criteria for our apparatus include (a) a thermally insulated cryogenic vessel with in/out access to let an inert gas flow inside the loading chamber at pressure higher than room pressure, thus avoiding contamination due to the atmospheric O_2 , CO_2 , and H_2O , and with an aperture for inserting the deposition capillary for the sample gas; (b) a direct measurement of the temperature near the diamond tips, to perform the deposition at the desired temperature conditions; and (c) the possibility to mechanically close the DAC before opening the vessel, to avoid both contamination and getting stuck due to the freezing of mechanical parts of the cell. The small and lightweight portable apparatus that was designed and built to match these criteria is shown in Figs. 1 and 2. A more detailed scheme of the apparatus, providing actual dimensions as well as sideways and vertical hindrances, can be found in Figs. S1 and S2 of the [supplementary material](#).

In principle, to cool down the cell is possible by using both a liquid nitrogen bath in an inert atmosphere and a closed-cycle cryostat (whose use is mandatory when the condensation temperature is below 77 K). In our case, as we worked mainly on acetylene and ammonia, the apparatus consists of a cryogenic vessel kept under inert gas purging (N_2 , Ar or He), where a specifically designed aluminum DAC holder is placed. The apparatus is designed for membrane Diamond Anvil Cells (mDACs),^{3,4} but it can work also for mechanical ones with suitable modifications. The box is covered by a Plexiglas cap, held between the poles of the DAC holder and the two handles of the whole structure, which allows us to easily remove it

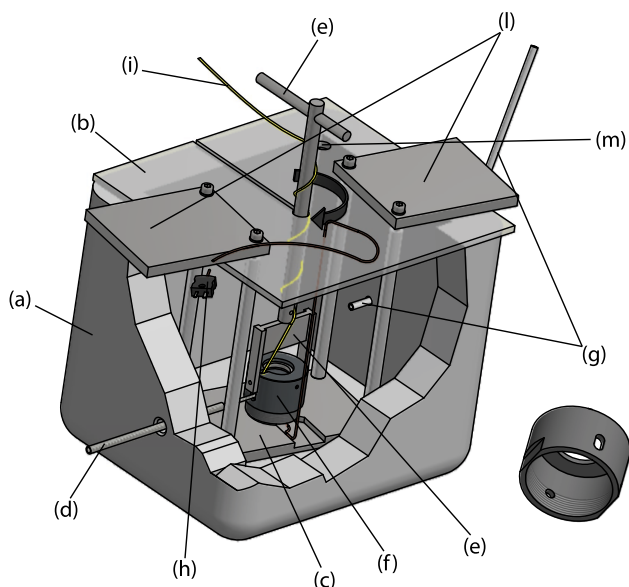


FIG. 1. A 3D graphical representation of the “spray-loading” apparatus: (a) cryogenic vessel, (b) transparent Plexiglas[®] cap, (c) DAC holder, (d) deposition capillary, (e) fork and fork handle, (f) DAC cover with eyelet for the capillary, (g) Rilsan[®] tube for purging gas (N_2 , Ar, He), (h) thermocouple wire and connector, (i) membrane capillary, (l) handles of the DAC holder and support, (m) inlet for liquid N_2 /outlet for purging gas overpressure. On the right bottom corner, a detail of the DAC cover with the dedicated oval opening for the deposition capillary to reach the sample chamber is shown. On the opposite side of the eyelet, a second, circular hole has been realized for ventilation. The black arrow around the fork indicates the rotation to screw the cover and mechanically close the DAC.

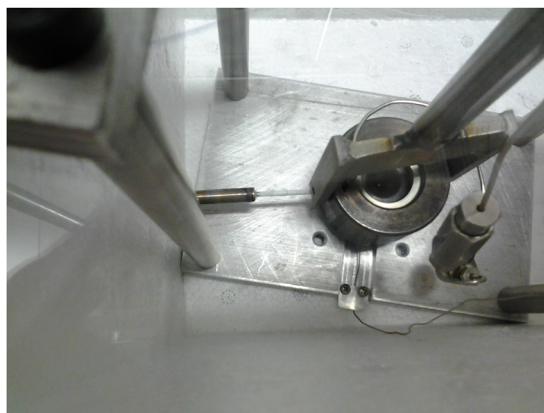


FIG. 2. Top view of the “spray-loading” apparatus before the use. The deposition capillary coated with the Teflon[®] tape and passing through the dedicated opening on the DAC cover is clearly visible, together with the fork for DAC mechanical closure and the thermocouple wire passing through its dedicated channel milled on the DAC holder. In the picture, the Nova-Swiss[®] adapter that connects the “membrane side” of the DAC, with its microvalve, to the external pressure driving system through a 1/16 in. stainless steel high-pressure capillary is also visible.

from the vessel once the loading procedure is completed. The DAC, slightly open with the diamonds spaced a few mm and the cover not completely screwed, is placed on the holder. On the metallic cover of the DAC (see details in Fig. 1), an eyelet has been mechanically perforated to let the deposition capillary reach the sample chamber through the spaced diamonds. The deposition capillary is a standard stainless steel 1/4-in. tube (internal diameter of 4 mm) welded to a thinner capillary (external diameter of 2 mm and internal diameter of 1 mm) where the tip hole has been closed by welding and a 1 mm gas outlet has been drilled perpendicularly to the flux direction so that, when the capillary is horizontally inserted into the DAC, the sample gas is sprayed directly over the bottom diamond (see Fig. 3). Purge gas flows inside the vessel through a 6 mm Rilsan[®] tube, while liquid N_2 is poured into the cryogenic vessel by a funnel through a dedicated hole drilled in the Plexiglas cap. During the procedure, the liquid is normally poured inside the vessel until it reaches the base of the DAC. The temperature near the sample chamber is monitored via a thermocouple blocked on the backing plate where the diamond is mounted and connected to an external reader. The thermocouple wire exits from the bottom of the DAC through a dedicated channel milled on the DAC holder. A fork is blocked to the DAC cover by two grub screws. The cover is not completely screwed on the lower semicell so as to let the diamonds spaced and to put the oval opening in the correct position for the capillary to enter the DAC. Being known the exact number of turns that puts the cover in the loading position, as well as how many turns are necessary in total to bring the diamond tips in contact with the gasket, it is possible to close the DAC by screwing the fork of the exact number of turns actually necessary, avoiding any risk of overpressure and diamond damages during the closure. In this way, once the loading is completed, the deposition capillary can be extracted from the cell and, as previously described, turning the fork by its external handle allows us to mechanically close the DAC; then, pressure can be remotely applied to the membrane by the pressure driving

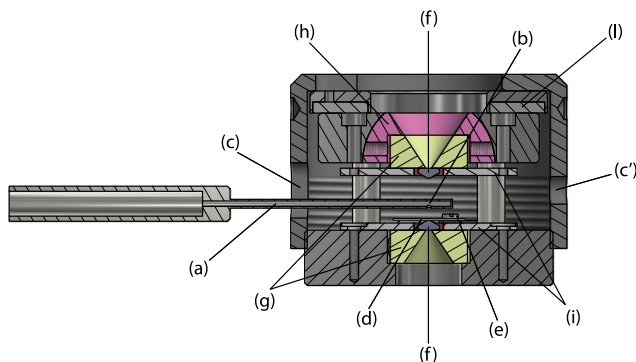


FIG. 3. Section view of the DAC during the loading procedure. (a) Deposition capillary, (b) gas-outlet on the deposition capillary, [(c) and (c')] deposition capillary entrance on the DAC cover and correspondent ventilation opening, (d) gasket, (e) thermocouple wire, (f) diamond anvils, (g) tungsten carbide seats for diamond, (h) tungsten carbide hemisphere, (i) backing plates, (l) stainless steel membrane.

system. The capillary that connects the cell membrane to the external pressure driving system passes through the same opening as the fork so as to allow a joint movement along the rotation axis of the cover during the mechanical closing of the DAC. Once pressure is applied to the membrane, the whole holder can be extracted from the vessel and the cell can be warmed up to room temperature, taking care of fluctuations in the membrane pressure due to rapidly increasing external temperature.

III. LOADING PROCEDURE

The aim of the spray-loading is to fill the gasket hole with the minimum possible amount of condensed gas sufficient to seal the sample, avoiding gasket closure. This procedure has to be done in a clean environment, under inert gas purging (in our case, N_2). Any solid component of the sample can be loaded in advance into the sample chamber using a microscope, and also small ruby chips⁵ (or other pressure gauges) are added prior to the start of the loading. The DAC is then fixed onto the aluminum holder, with the diamonds spaced and the cover not completely screwed, this way allowing the insertion of the deposition capillary through the dedicated opening on the DAC cover. The first step of the procedure is to purge the cryogenic vessel, an operation that takes 5-10 min at nitrogen pressure of maximum 1 bar. Once the atmosphere is replaced by inert gas, the DAC can be cooled down to the deposition temperature. We use liquid nitrogen as a thermal reservoir because it is cheap and non-hazardous and allows us to condensate several kinds of gases. Liquid N_2 is slowly poured into the cryogenic vessel, cooling the DAC holder and the bottom part of the DAC, which is in direct contact with the aluminum holder. During all the stages of the procedure, in order to prevent the obstruction of the deposition capillary due to sample condensation, a weak flux of He at room temperature is maintained through the line while the temperature decreases: boiling and melting temperatures of He are indeed lower than the liquid nitrogen temperature. Once the temperature for the desired condensation is nearly to be achieved, the flux of He is reduced or even stopped and the flux of the gas to be sprayed onto the

diamond is opened (with injection pressure out of the bottle being less than 0.1 bar). The amount of gas that passes through the deposition capillary is very small, with most of it condensing directly on the cold cell. Very low flux is ideal for this method: a strong flux could indeed likely flush away ruby chips or other solid components out of the sample chamber and thus has to be avoided. The whole procedure is performed under hood to minimize any risk. Once the deposition is completed, the flux is closed and the deposition capillary is extracted. Besides depositing unnecessary large amounts of sample and risking the blockage of the mechanical parts of the cell due to the freezing of the sample, keeping on fluxing during this step may result in warming the deposited sample, thus increasing the risk of losing it due to undesired melting or boiling favoured by the higher temperature of the incoming gas. The DAC is then manually closed by turning the fork, which brings the top diamond in contact with the gasket. At this point, the DAC is rapidly cooled down to liquid nitrogen temperature (77 K) while external pressure is applied to seal the sample chamber. Once the desired membrane pressure is applied, the DAC can be extracted from the cryogenic vessel and warmed to room temperature. The whole procedure lasts roughly 1 h and is much faster than other loading techniques.

IV. EXAMPLES OF APPLICATION OF THE SPRAY-LOADING SYSTEM

The spray-loading technique, originally developed to be used in combination with a closed-cycle cryostat, allowed us to load several water/hydrocarbon mixtures.^{6,7} This method was extremely time-demanding due to the complex procedure for assembling the closed-cycle cryostat, mounting the DAC inside the cryostat, and pumping the whole system. Furthermore, access to the DAC was limited and every failed loading attempt would have meant to restart the whole complex procedure from the beginning. The new version of this apparatus, described in Secs. I–III, was instead developed to be simpler and easy-to-use, making the preparation step faster. The efficiency of the loading procedure can be highlighted by the IR spectra because, by probing all the samples at once, they provide information about any possible sample contamination.

Acetylene is the simplest alkyne, a highly unstable molecule that requires special care to be handled, because it is explosive (especially if pressurized) and highly flammable. Commercial acetylene is indeed supplied and stored dissolved in acetone. The loading of C_2H_2 (Rivoira, purity of 99.6% and further purified prior to loading⁶) is performed by realizing the deposition between 195 and 185 K since the acetylene melting point is at about 191 K. In addition, special care must be taken to avoid that the pressure applied during the closure of the DAC would overcome the relatively low pressure reaction threshold for pure acetylene to polymerize (about 4 GPa at room conditions).⁶ In Fig. 4, a Fourier-transform infrared (FTIR) spectrum of a sample of acetylene loaded with *spray-loading* is shown. The spectrum is dominated by the infrared allowed ν_3 (antisymmetric C–H stretching) and ν_5 (antisymmetric C–H bending) modes, respectively, at 3250 and 750 cm^{-1} and by the $\nu_4 + \nu_5$

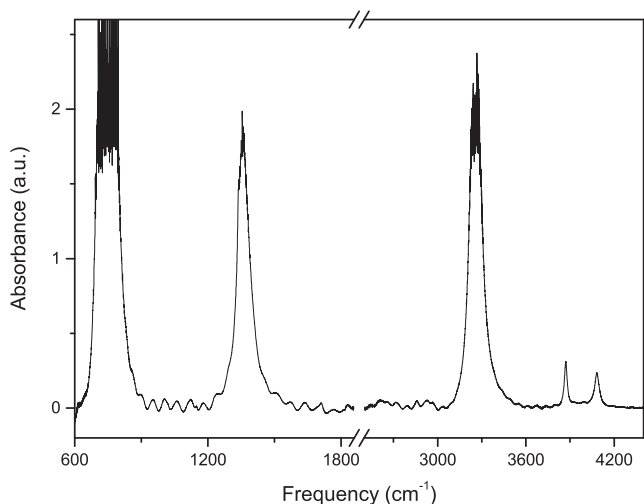


FIG. 4. FTIR spectrum of as-loaded liquid acetylene at pressure 0.3 GPa and room temperature. The frequency axis break excludes the frequency region where the saturating absorption of the diamond anvils occurs.

combination mode at about 1365 cm^{-1} (where ν_4 refers to the C–H symmetric bending). All these modes are out of scale. The combination bands for acetylene are visible at much higher frequency. No traces of atmospheric water or CO_2 can be detected in the spectrum, attesting for the complete absence of contamination in the loaded sample. We loaded with this method several samples of pure C_2H_2 and C_2H_2 in the presence of 3D and 1D pure SiO_2 zeolites for studying its polymerization reaction under extreme confinement.^{8,9}

Ammonia is irritant and corrosive. In fact, as a corrosive species, ammonia could be dangerous to load for the typical cryo-loading instruments, aside from being dangerous also for some components of the DAC (Cu components especially, such as copper rings used for mounting anvils on the backing plates, which need to be protected by using resins or specific glues). In our experiments, ammonia was loaded by performing the deposition at about 195 K, thus just below the melting point. In this case, unlike in the acetylene loading, no special care is needed for what is concerned with the pressure of the DAC after the loading and during the warming to ambient temperature because of the chemical stability of pure ammonia. In Fig. 5, a FTIR spectrum of a sample of NH_3 loaded by the spray-loading technique is shown. The inset picture shows the aspect of the sample, and two ruby chips are visible on the edge of the gasket. The spectrum is dominated by the out-of-scale ν_2 (symmetric N–H bending, 1060 cm^{-1}), ν_1 , ν_3 (symmetric and doubly degenerate N–H stretching, at about 3300 cm^{-1}), and ν_4 (doubly degenerate N–H bending, 1630 cm^{-1}) infrared allowed modes. The combination bands of NH_3 , $\nu_2 + \nu_3$, and $\nu_3 + \nu_4$ are visible at higher frequencies.¹⁰ No evidence of the contamination of the as-loaded sample due to atmospheric water or CO_2 can be seen in the spectrum. We loaded with this method several samples of pure NH_3 and heterogeneous mixtures of NH_3 in the presence of graphene oxide^{10,11} or red phosphorus for structural and reactivity studies.

The spray-loading technique and apparatus can be profitably used to load mixtures of species with very different

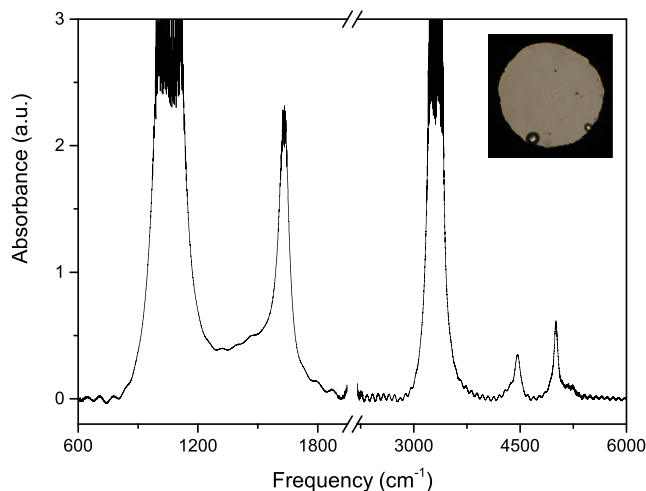


FIG. 5. FTIR spectrum of as-loaded liquid ammonia in the DAC at pressure 0.5 GPa and room temperature. In the inset, the sample aspect after the loading is shown. Two round-shaped ruby chips are clearly visible along the edge of the gasket hole. The frequency axis break excludes the frequency region where the saturating absorption of the diamond anvils occurs.

melting and boiling points. In our laboratory, we developed a dedicated deposition line for mixtures containing water, and recently we have studied carbon dioxide/water mixtures. The DAC was prepared with rubies and cubic Boron Nitride (c-BN) as independent pressure gauges and then mounted on the spray-loading aluminum holder. Carbon dioxide (Rivoira, purity of 99.99%) served at the same time as one of the mixture components and as a gas carrier to gurgle through a glass bottle of ultra-pure water so as to transport small water droplets with its flux. The two components did condense directly into the sample chamber when the temperature of the DAC reached 193 K. For cooling down the DAC, we used a liquid nitrogen bath. During the whole procedure, a small flux of He was maintained through the line so as to keep the deposition capillary warm: in the case of this mixture, in fact, an additional issue is related to the presence of water in a very low temperature environment. Water could freeze along the line, resulting in a stuck of the small aperture of the deposition capillary. In addition, the deposition capillary itself, the bottle of water, and most of the loading line are kept under moderate heating during the whole procedure. At the end of the deposition, the top diamond is directly frozen down using liquid nitrogen prior to the mechanical closing of the cell, so as to avoid that a temperature gradient on the diamond tips could result in an undesired melting of the mixture while sealing the sample chamber. Figure 6 reports a FTIR spectrum of the mixture of carbon dioxide and water loaded as described. The infrared absorption modes of water (bending, 1645 cm^{-1} , and stretching, 3300 cm^{-1}) dominate the spectrum. As the CO_2 phase I is concerned, the saturating bending (around 660 cm^{-1}), the stretching (around 2345 cm^{-1}), and the combination $\nu_3 + \nu_1$, $\nu_3 + 2\nu_2$ (with major peaks at 3610 and 3730 cm^{-1}) regions are clearly visible. All these absorption bands are out of scale. More details about the assignments can be found in Refs. 12 and 13. The picture in the inset shows the aspect of the sample. Pressure gauges (round-shaped rubies and a triangle-shaped crystal of c-BN) are clearly visible in the sample chamber.

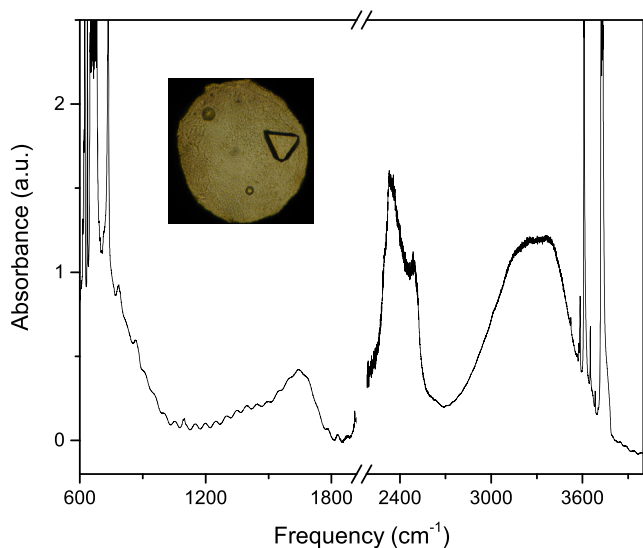


FIG. 6. FTIR spectrum of the as-loaded mixture of carbon dioxide and water in the DAC at pressure 2.0 GPa and room temperature. In the inset, the sample aspect after the loading is shown: two ruby chips and a crystal of c-BN are visible. The frequency axis break excludes the frequency region where the saturating absorption of the diamond anvils occurs.

V. CONCLUSIONS

We have discussed the construction criteria of a novel, useful apparatus to perform cryogenic deposition of gases inside the DAC. This method can be profitably used for potentially hazardous samples (explosive, toxic, or corrosive ones with condensation temperature above 77 K) and for the loading of complex mixtures of gases and chemical species with very different melting and boiling points. Spray-loading allowed us to obtain several samples of acetylene, ammonia, and ethylene in the DAC simply by the condensation of a small quantity of gas directly inside the sample chamber. The method allowed us to load pure gaseous samples and also composite samples (solid and fluid mixtures, where the solid components were loaded before the DAC was placed in the cryogenic vessel). The loading procedure is fast and efficient and, due to the small dimensions and the portability of the experimental apparatus, can be performed under hood without any risk. Spray-loading has been demonstrated to be a suitable and useful technique for

the loading of hazardous samples and very complex mixtures of different species.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for a complete description of the experimental equipment with sizes and a list of the fabrication materials.

ACKNOWLEDGMENTS

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