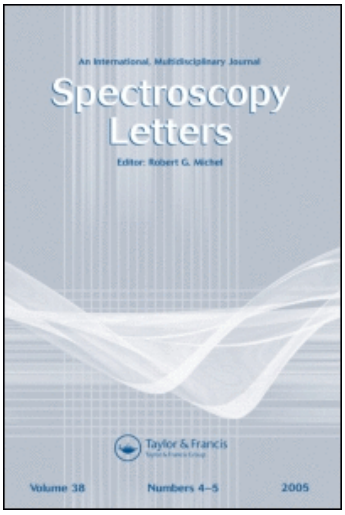

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Studies of the Desolvation Mechanism of the Thermospray (TSP)—New Explanation on Analytical Sensitivity Enhancement with TSP Coupled HPLC-FAAS

Peter P. Chang[a]; James W. Robinson[a]
[a] Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana

To cite this Article Chang, Peter P. and Robinson, James W.(1996) 'Studies of the Desolvation Mechanism of the Thermospray (TSP)—New Explanation on Analytical Sensitivity Enhancement with TSP Coupled HPLC-FAAS', Spectroscopy Letters, 29: 8, 1469 — 1480
To link to this Article: DOI: 10.1080/00387019608007138
URL: http://dx.doi.org/10.1080/00387019608007138

SPECTROSCOPY LETTERS, 29(8), 1469-1480 (1996)

STUDIES OF THE DESOLVATION MECHANISM OF THE THERMOSPRAY (TSP) — New Explanation on Analytical Sensitivity Enhancement with TSP Coupled HPLC-FAAS

Peter P. Chang and James W. Robinson*
Department of Chemistry
Louisiana State University
Baton Rouge, Louisiana 70803

ABSTRACT

Previous cadmium speciation studies using a modified thermospray (TSP)-coupled-HPLC-Flame AAS system gave significant improvements in limits of detection (LOD). Experimental data also revealed that a smaller capillary tip orifice size and a larger capillary internal diameter (ID) providedbetter LOD and relative standard deviation (RSD). Further studies to understand the desolvation mechanism inside the TSP capillary generated a new concept of the possible desolvation process occurring inside the heated TSP capillary. The separated components in the HPLC efficient were preconcentrated in a series of concentrated solute plugs producing concentrated plugs of free atoms and hence increased absorption.

INTRODUCTION

Moderate sensitivity improvements with the application of TSP as the interface for LC-MS, LC-ICP, and LC-AAS were reported by several researchers who proposed that a certain desolvation process occurred inside the TSP capillary (1, 2, 3, 4, 5).

Koropchak et al. reported that, at high solvent flow rate and controlled heating, the aerosols appeared dense with narrower distribution of particle sizes. The heated droplets rapidly began to desolvate and concentrate the less volatile analytes, providing higher analyte transport rate and yielding enhanced detection (2).

Mayar et al. also observed the desolvation phenomenon (3). Droplet size related aerosol transporting efficiency, the desolvation rate, and the vaporization rate of the dried analyte particles after desolvation were studied. The results showed that the TSP nebulizer aerosol generated a smaller mean particle diameter compared to that of the pneumatic nebulizer. The numbers of smaller particles increased as functions of the elevations of TSP temperature and sample solution introduction rate.

Vestal et al. proposed a " soft-ionization" mechanism (6) inside the TSP capillary where a radial temperature gradient existed to cause a higher liquid temperature near the capillary wall than the central stream. Therefore, more volatile solvent was first vaporized around the wall with the less volatile analyte remained as liquid in the central stream. At a given flow rate and with adequate TSP thermal energy input, nearly complete vaporization of the solvent preconcentrated the analytes and provided a high vapor pressure. The latter brought a great pressure drop between the TSP tip and the atmosphere which caused further shattering of the liquid/vapor mixture into a jet spray of very fine droplets from the emerging HPLC effluents.

Vestal' s desolvation assumption was based upon the Leidenfrost phenomenon noticed in 1756 (7). When a drop of liquid is dropped on a hot plate, it evaporates rapidly . Above a certain temperature, the Leidenfrost Temperature, the liquid could no longer wet the plate, but danced and bounced and was isolated from the hot plate by a thin layer of vapor. The Leidenfrost Temperature of water is 185-325°C, depending upon the material and surface structure of the hot plate.

A superheated aerosol/vapor mist jet spray could be generated consisting of a coaxial solute concentrated central cone and solvent concentrated edge cone. In such ideal spray, the solute should be concentrated in the spray center, while the solvent vapor layer around the central cone could be eliminated by skimming. However, this did not appear to be the case in our ultra trace metal speciation research using HPLC-TSPGraphite Furnace AAS. With a skimmer solvent removal system, the furnaces were still burned by considerable amounts of aqueous solvent in the spray center. The dried, soluteconcentrated, central aerosol cone was not detected.

Vestal' s desolvation mechanism has been widely accepted in the LC-MS field. However, the theory includes some contradictions. Even if the solute and solvent were separated during the desolvation process inside the capillary considering the great pressure drop when the effluents emerge from the TSP tip, they would probably have remixed during the shattering of the liquid vapor to fine droplets. A skimmer of a 1-3 mm ID pinhole removed more than 99% of original solutes and aqueous solvent from the HPLC effluents which resulted in no absorption signal at all but still quickly burned the furnaces(8). Such loss of sensitivity has been observed by other workers.(9, 10, 11).

A new TSP was built with larger ID capillary and smaller tip orifice. It was used to couple an HPLC to Flame AAS for cadmium speciation. A 1,000 fold absolute sensitivity increase was observed (12). The desolvation mechanism inside the capillary was reexamined. Large amount of analytes usually accumulated inside the superheated TSP stainless steel capillary (13) which eventually clogged and destroyed it. Such accumulation could be eliminated by washing the capillary with acetic acid injection regularly. During such capillary re-generation process, extremely strong signals of the metal accumulated could always be detected by AAS. It was believed that the solute was accumulated and concentrated on the internal wall of the heated capillary by adsorption, and was then washed out of the TSP to generate strong signal by acid desorption.

In reality, the Leidenfrost theory applies to pure solvents but not solutions. When a solution is dropped onto a hot plate, only solvent is vaporized, but solute will be dried onto the surface of the hot plate as residue. The above concentration phenomenon indicated that the solute could be separated from the solvent by adsorption to the internal wall of the heated capillary, rather than being concentrated in the central stream of the effluents. A similar phenomenum may occur when the sample solution passed through a very hot TSP capillary (>715°C at a 130-W power input). The HPLC effluents adsorption onto and desorption from the internal wall of the hot capillary could play a role of solute concentration to generate much stronger analytical responses.

A series of tests was designed to examine the behavior of TSP capillary with different ID and tip orifices sizes. The experimental data showed that, at a given volume flow rate of HPLC effluents and energy input, the smaller the capillary tip orifice and the larger the capillary ID of the TSP, the higher the analytical sensitivity and the better the reproducibility (12). In addition, over a

wide power input range (100-180 W), absorption signal responses independent to the TSP heating power input were observed with narrowed tip orifice on thicker ID TSP capillary. A new concept of the desolvation process occurring inside the TSP capillary can therefore be proposed from these experimental observations.

EXPERIMENTAL

A. Equipment Used

[1] Metal Detector: Perkin-Elmer Flame Atomic Absorption Spectrometer 370A with 10 cm single slot burner head.

[2] Radiation Source: Perkin-Elmer cadmium hollow cathode lamp operated at 5-mA and 12-V, with strongest cadmium resonance line at 228. 8-nm monochromatic wavelength.

[3] Solvent Delivery System: Rainin Rabbit HPLC solvent delivery sums with 5. 0-mllmin maximum flow rate single piston head.

[4] Pulse Dampener: Alltech Free Flow pump pulse dampener with 1/4" to 1/16" fitting converter for column-pump connection, and an old 150x4.6 mm, 3 Fm HPLC column.

[5] Fractional Collector: 5.5 test tubes/second collecting rate for spray collection.

[6] Sample Injector: Rheodyne 7125 injector with 100 Wl sample loop except specified.

[7] Capillary Tubing Cutter: Alltech stainless steel tubing wheel-cutter with trapezoidshaped cutting wheel modified in house.

[8] Recorder: Linear Instrument Chart recorder.

[9] Water Re-distiller: Pyrex condenser and flask.

[11] TSP Nebulizer: 150-W "firerod" electric heating cartridge by Watloo, with 1/16" OD, 0.005", 0.007", 0.01", 0.02", and 0.03" ID stainless steel capillary spray chamber by Alltech.

[12] TSP Constant Power Supply: The circuit was consisted of a constant high ampere transformer combined with two step-down transformers and a 1-100% variac. The variac gave a continuously fine voltage adjustment with 0. 14-V and 0. 01-A for 1% variac variation.

B. Samples and Reagents Used

[1] Standard Solution: 200., 100., and 50.0 ppb $CdCl_2$ freshly prepared from 1,000. ppm standard made by dissolving 1.000 gram cadmium metal in HCl acid and diluting to 1.000 liter.

[2] Solvents: Re-distilled lab deionized and distilled water to remove trace impurities.

[3] Washing Solutions: 10. % nitric acid and 10. % HCl acid (v/v) for burner assembly cleansing; 0.50 mM citric acid for TSP capillary regenerating; methanol, THF, and DCM for HPLC columns regeneration. 20. % nitric acid for HPLC assembly frits and fittings washing.

[4] Flame: Air-acetylene oxidizing flame was used.

C. Experimental Procedures

The same TSP nebulizer interfaced HPLC-flame AAS system for cadmium speciation studies in human urine was again used and optimized by the same procedures (12). The data and observations obtained in TSP optimization were used to develop a new desolvation mechanism. Additional preparation procedures for the experiment are described as follows.

[1] Examinations on TSP Spray Pattern for Vestal' s Assumption

Vestal' s desolvation mechanism predicted the generation of a coaxial, double cone, spray for separated solute and solvent, but the TSP interfaced HPLC-Graphite Furnace AAS for metal speciation did not detect these(8).

A simple experiment was conducted to study this effect. Two small beakers with different sizes were coaxially arranged one in another. The ID ' s of the two beakers were chosen to give the same crosssectional entrance areas for equal vapor collection in unit time. The TSP was then mounted up-sidedown directly above the beakers with a distance from the TSP tip to the beakers adjusted to accommodate the entire spray. After the TSP reached its optimum operating condition at 110-W energy input, 1.00-ml of 20.0-ppm cadmium chloride was flow-injected into the TSP. The aerosol of cadmium chloride from the TSP tip was collected, and the concentrations of the solute in the beakers were measured with TSP interfaced HPLC-Flame AAS. The results showed identical concentrations of cadmium chloride in the two beakers, indicating that the solvent and the solute were not separated upon emerging from the TSP, which in turn proved that Vestal' s ideal spray was not observed for solutions.

[2] Solute Transporting Rate in Unheated TSP Capillary

In order to determine whether there was an adsorption or desorption process for solute being transported through a heated capillary, the solute transportation rate inside a cold capillary was needed for comparison.

With a solvent volume flow rate at 2.00-ml/m, 0.10-ml sample should take 3 seconds to pass the capillary completely. Due to the possible diffusion in between the solute and the solvent, such transportation might take longer time for the some volume of solute. 0.10-ml of 0.5-M HCl acid was then injected into an unheated TSP capillary at 2.00-mllmin flow rate. The acidic solution was collected at the tip of TSP simply with a pH test paper. Interestingly, 0.10-ml of acid yielded red color on the paper for 6 seconds, which confirmed the acid diffusion into the solvent. If such diffusion of the solute disappeared to result higher solute transportation rate with heated TSP, then the solute adsorption process inside a heated TSP capillary could be confirmed.

[3] Solute Transportation Rate in Heated TSP Capillary

The concentration process inside a heated TSP might be the result of solute adsorption on to the internal surface of a hot TSP capillary. Studies of the solute transportation rate in a heated TSP capillary was carried out by collecting the testing analytes eluted from a heated TSP capillary at normal operating conditions and measuring the solute eluting rate. A fractional collector with 5.5-tubeslsec collecting rate was used. The TSP was composed of a 150-W heating cartridge equipped with 75 plum tip orifice on a 0.02" ID capillary, and was heated at 110-W. The TSP nebulizer was directly connected to the HPLC pump, and was installed face-down on the collector sampling arm to spray the aerosol into 100 rotating test tubes. The TSP tip was precisely aligned to the center of each rotating test tube, and was kept minimum distance to the tubes so that the sample effluent loss would be minimal. The test tubes were cleaned and rinsed thoroughly. With the TSP operating at its optimum conditions, 0.10-ml of 20.0-ppm cadmium chloride was injected with a solvent volume flow rate at 2.00-mllmin. The collector was turned on at the same time the sample was injected. The effluent spray collected in the test tubes were then diluted with 1.00-ml of purified water, and the cadmium concentrations were measured with HPLC-TSP-Flame AAS.

RESULTS AND DISCUSSION A. Analyte Adsorption/Desorption inside Heated TSP Capillary

As indicated earlier the Leidenfrost phenomenon probably may not apply to solutions. Inside the TSP capillary, with the fast-moving solution, the situation might be a little different from a flat plate. At lower capillary temperatures, an equilibrium between adsorption and desorption

may exist between the solution flow and the capillary internal surface. At higher capillary temperatures, complete sample desolvation may occur, then the desolvated analyte may be adsorbed onto the internal surface of the capillary. This slows the analyte migration speed, and causing a temporary analyte concentration increases at the capillary internal surface. With the continuously flowing HPLC solvent inside the capillary, fresh solvent desorption will eventually overcome the temporary solute adsorption onto the TSP capillary internal surface. The accumulated and concentrated analyte is then be ejected from the capillary tip. An increase in solute transportation rate in unit time increases the signal peak heights with reduction on the peak widths, resulting in improved signal noise ratio.

At the flow rate used, 0.10-ml of sample should be equally distributed into 17 or more test tubes of the collector. Interestingly, however, with 0.10-ml of cadmium chloride passing through the heated TSP capillary at 2.0-ml/lmin HPLC solvent flow rate, the result showed very little cadmium was collected in the first 16 tubes; but significant amount of cadmium was detected from the collections in tubes from tube No. 15 to tube No. 21. After tube No. 22, the signals of cadmium contents in the following tubes were dropped almost to zero again. Similar results were obtained with six repeated tests.

Significant absorption signals were detected only after tube No. 15. A maximum was observed at tube No. 19 which indicated that most of the cadmium solute was ejected at that point, and disappeared after tube No. 22.

The cadmium mostly collected in the six test tubes indicated that the entire analyte eluted from a heated TSP capillary within about one second (-1.2 second), rather than the 3 seconds expected from an unheated TSP capillary. This seemingly indicated that the metal analyte was somewhat preconcentrated inside the heated capillary before emerging. Little analyte found in the first 14 tubes indicated a migration delay of the majority of analyte inside the hot capillary. The delay was up to 2 seconds. Within these two seconds, the solvent vaporized and separated from the solute, passed the capillary and emerged first, while the solute was plated onto the internal surface of the hot capillary.

B. Proposed Desolvation Mechanism in TSP Capillary

Based on the results, a new sample desolvation mechanism inside the heated TSP capillary has been proposed. The process of the mechanism are discussed.

[1] The Analyte Desolvation Processes

Upon entering the hot zone of the TSP capillary, the very front of the sample first vaporizes, the solvent which stays in the center of the capillary; while the solute deposits onto the capillary internal wall. As sampling proceeds the solute spreads into a layer above the heated internal surface. More desolvated solute plates onto the top of the previous solute layer. A hollow "solute tube" forms temporarily increasing in thickness progressively forming a solute tube.

Meanwhile solvent vapor is continuously created, the diameter of the tip is decreased and the vapor pressure increases. Finally the system 'explodes' ejecting accumulated solute, as a plug.

This was an effective desolvation process. The "solute plug" explains why the entire 0.10-ml analyte was detected within about one second from a heated TSP capillary rather than expected 3 seconds, and why the TSP nebulizer resulted in intensified signal peaks compared to other nebulizer interfaces used in LC-MS, LC-ICP, and LC-Flame AAS.

[2] Effect of Capillary ID on Desolvation Efficiency

For the TSP nebulizers, with the same 75 Gem tip orifices, the best signals were obtained using 0.02" ID TSP capillaries, while the worst were observed using 0.005" ID capillary (12). With the same volume flow rate, the linear velocity (in a 005' ID capillary) capillary was 16 time faster than that of 0.02" ID. The sample residence time inside the 0.005" ID capillary was, therefore, 16 time shorter than that of 0.02" ID. At a certain power input, the thermal energy was removed by fast-moving solution, and the desolvation process was far from completion inside the 0.005" ID capillary compared with that of 0.02" ID. On the other hand, the sample movement inside the capillary was the product of its linear velocity and its solvent radial vaporization rate. The radial vaporization rate inside the 0.005" ID capillary was much suppressed by its narrow diameter. The desolvated solute spread and re-mixed with its solvent inside the capillary by much faster linear velocity of the sample solution. The " solute tube" and the " solute plug" was not quite formed, and incompletely desolvated sample did not produce enhanced signals.

With 0.02" ID capillary, however, the radial vaporization rate was not so suppressed and the solution moved much slower. The thermal contact between the sample and the capillary internal wall was better, the sample solvent separation from the solute was better, and the solute concentrated " solute plug" resulted from better desolvation results in enhanced detection sensitivity.

[3l Effect of Tip Orifice Size on Desolvation Efficiency

With the same volume flow rate, TSP capillary equipped with narrower tip orifice (75 Am) would result in much higher sensitivity than the TSP capillary with larger tip orifice or without narrowed orifices (12).

Such phenomenon can be explained as the better desolvation process resulted from the higher back vapor pressure. The smaller the tip orifice on the TSP capillary, the higher the back pressure of the solvent vapor, the shorter the " solute tube" length, the higher the concentration in the " solute plug", the faster the solute transportation rate, and the stronger the signal.

In addition, the smaller the tip orifice, the higher the vapor pressure inside the capillary, the greater the pressure drop between the tip of TSP capillary and the atmosphere, the stronger the shattering effect on aerosol formation, the finer the aerosol droplet sizes, and the better the atomization efficiency, which in turn would result in much higher analytical sensitivity and better reproducibility.

[4] Observations Supportive to the Desolvation Mechanism

There were different observations that may support the proposed mechanism as follows.

(a) Effective Desolvation Zone in the Capillary

With the same heating length, the thermal contact area between the capillary internal surface and the sample solution was four time larger with 0.02" ID than with 0.005" ID. Taking the 16 time slower linear velocity of the sample solution into consideration, the desolvation efficiency of the sample in 0.02" ID capillary should be much higher than in 0.005" capillary.

If adequate thermal energy could effectively convert all the liquid sample into solvent vapor and dried solute aerosol inside the capillary, then the entire capillary heated region would be constantly kept at higher temperature by excessive thermal energy. If the linear velocity of solution was high it quickly removed most of the heat, as in 0.005" ID capillary. The heating time would be very brief and the heated region would very small. This may be confirmed by examining the color change on the external surface of used capillaries.

CONCLUSIONS

This result of the study of the TSP desolvation mechanism now can be summarized as follows:

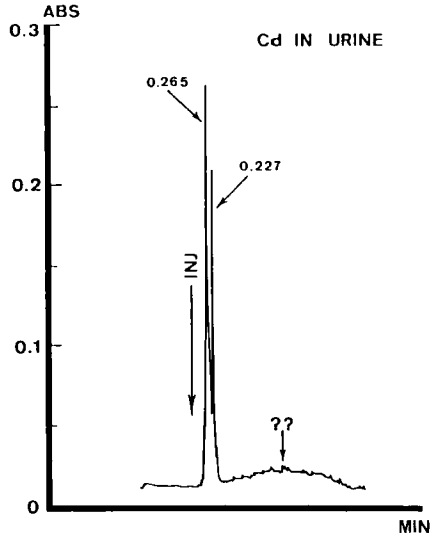

Figure 1. The HPLC chromatogram of the first speciation separation of trace cadmium compounds in human urine with the new TSP nebulizer interfaced HPLC-flame AAS system. The 0.265 absorbance of the first peaks revealed a 10^3 fold sensitivity increase. Note many complexed cadmium compounds.

A. The Vestal's desolvation mechanism could be modified. Under our experimental conditions that Vestal' s ideal, coaxial, separated solute and solvent dual cones did not usually occur. The desolvated solute from the sample solution tended to plate onto the internal surface of the heated TSP capillary, but never stayed in the central stream .

B. Above the Leidenfrost Temperature of the solvent, with appropriate TSP energy input and solvent volume flow rate, adequate thermal energy transferred to the liquid sample completely vaproized the sample solvent. The desolvated solute tends to partially plate on the internal surface of the capillary forming a "solute tube". The solvent vapor formed a solvent front. The "solute tube" increase in thickness layer by layer due to new deposits of desolvated solute until its thickness reached the maximum. When very high back pressure built up by the solvent vapor, closing it tubular end to form a "Solute plug". The solvent front is separated from the solute and emerges from the capillary followed by the solute-enriched " solute plugs . The latter was ejected from the capillary tip orifice into the base of the flame burner.

This desolvation process results in a solute-enhanced spray aerosol with a series of reconcentrated solute components from HPLC effluents. At the end of the capillary, the narrowed TSP tip orifice provides a large pressure drop between the orifice and the atmosphere supplying adequate mechanic power to shatter the almost pure and "dried solute" to fine droplets for the high atomization efficiency. In addition to the desolvation process, the TSP enjoys essentially no sample loss during the sample transportation to the atomizer (14,15), which accounts for a great sensitivity increase and 1,000 folds of absolute sensitivity increase compared to the analytical ability of conventional flame AAS.

(b) Signal Peak Appearances

The direct measurements of the signal peak width may be another criterion to confirm that solute enrichment occurred inside the capillary before it was ejected from the tip orifice.

Figure-1 shows a small group of very sharp cadmium absorption peaks with about one second widths for 0.10-ml injection under the same TSP operating conditions. this actually confirmed that the TSP nebulizer did effectively desolvate the sample solution, enriched the analytes, delayed the analyte migration inside the capillary but sped up the analyte transportation rate in unit time, and therefore enhanced the signal peak height which resulted in the detection sensitivity increase.

BIBLIOGRAPHY

1. M. L. Vestal, Anal. Chem., 1984, 56, 2590
2. J. A. Koropchak, D. H. Winn, Trends in Anal. Chem., 1987, 6(7), 171
3. G. A., Mayar, S. A. Schwartz, Spectrosc. Acta., 1986, 1287
4. M. L. Vestal, G. J. Fergusson, Anal. Chem., 1985, 57, 2373
5. J. A. Koropchak, Anal. Chem., 1990, 62, 484-489
6. M. L. Vestal, Int'l J. M. S. & Ion. Phy., 1983, 193
7. J.G. Leidenfrost, De Aquae Communis Nonnullis Quantitatibus Tractatus, Duisburg am Rhein, 1756
8. P.P. Chang, Ph. D. Dissertation, Ch-2, 32-79, LSU, 1991
9. P.Arpino, M. A. Baldwin, F. W. McLafferty, Biomed. Mass. Spectrom., 1974, 1, 80
10. J.D. Henion, Anal. Chem., 1978, 50. 389

11. F.R. Sugnaux, D. S. Skrabalak, J. D. Henion, J. Chromat., 1983, 264, 357

12. P.P. Chang, J. W. Robinson, Spectroscopy Letters, 1993,p-

13. D.S. Choi, Ph. D. Dissertation, LSU, 1989

14. D.S. Choi, J. Robinson, Spectroscopy Letters, 1987, 20(4)., 375

15. D.S. Choi, J. Robinson, Spectroscopy Letters, 1988, 21, 337

Received: July 1993
Accepted: June 6, 1996