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*Original Paper*

# Direct injection nebulizer with replaceable capillary for micro samples analysis by inductively coupled plasma-optical emission spectrometry

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**Abstract.** The analytical performance of a low cost direct injection high efficiency nebulizer (DIHEN) with replaceable capillary is evaluated and compared with a high efficiency nebulizer HEN-cyclonic spray chamber arrangement for sample introduction at lower solution uptake rates in inductively coupled plasma optical emission spectrometry (ICP-OES). The system allows the use of a replaceable capillary and optimization of the aerosol generation. The study was performed in terms of the main analytical figure of merits (i.e., sensitivity, limits of detection and signal stability) for plain water solutions and matrix effects caused by nitric acid and sodium in ICP-OES. In general, the DIHEN with replaceable capillary offers better sensitivities than the HEN-Cyclonic system and for some elements, improved detection limits (DL) in the range of 1.1–3.8 $\mathrm{ng \cdot mL^{-1}}$ for Ba, Mg, Zn 206.2–200 nm and Zn 213.8–856 nm were obtained. Strontium's DL was comparable with both systems and those for Cd and Mn were slightly worse. Short-term precision for this unit is not as good as the HEN-Cyclonic system, but being less than 2%, it can still be considered acceptable. It was more susceptible to changes in matrix composition, being ca. 18% the acid depressive effect and 7% due to sodium with the DIHEN compared to the conventional nebulizer-spray chamber arrangement (13 and 3% acid and sodium depressive effect, respectively). The utility of the developed unit is explored analyzing three certified materials (bovine liver, rice and wheat flours) and the experimental results are within the certified values. The ability of the DIHEN with replaceable capillary to analyze real micro samples (samples reconstituted in 150 μL deionized water) was demonstrated by the determination of Ca, Cd, Cu, Mg, Mn, Sr, and Zn in individual scorpion venoms samples. One of the main advantages over other arrangements is that it can be easily constructed in the laboratory.

**Keywords:** Replaceable capillary; direct injection; ICP-OES

Despite the advances made in instrumentation, the introduction of sample to the plasma in inductively coupled plasma optical emission spectrometry (ICP-OES) persists as the weakest area in this technique.

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Therefore, it is necessary to continue investigating in this area.

The introduction of liquid samples into plasma is the most common procedure of sample introduction in inductively coupled plasma (ICP) spectrometry. Sample introduction is the result of various processes, mainly aerosol generation, transport and filtering and, when the solvent vapor load have to be reduced, desolvation. Each process plays a role in determining or changing the aerosol characteristics and, hence, influencing the final analytical performances.

It is well known that the liquid sample introduction system consists of a nebulizer, mainly of the pneumatic concentric type. The aerosol produced at the tip of a pneumatic nebulizer is termed the primary aerosol. The aerosol generated in this way is introduced in the spray chamber whose mission is to filter the aerosol. Some pneumatic nebulizers employ an impact bead, positioned a short distance from the nebulizer tip, to further shatter the primary aerosol into a finer spray known as the secondary aerosol. As the droplets pass through a spray chamber, solvent evaporates from the surface of droplets and larger droplets settle out of the aerosol stream, shifting the droplet size distribution to smaller diameter. The resulting aerosol is referred to as the tertiary aerosol [1–7]. This arrangement, conventional nebulizer-spray chamber, suffers from a number of well-known drawbacks such as high sample consumption (typically 1–2 $\mathrm{mL\,min^{-1}}$), low analyte transport efficiency (1–2%) to the plasma, memory effects, contributes significantly to matrix effects and generates significant amount of waste [8].

The development of devices [9–25] dedicated to work at very low liquid flow rates (i.e., of the order of several tens of microliters per minute) has opened up the possibility of easily analyzing samples using ICP-OES in which the amount of sample is limited. These developments also allow the efficient coupling of separation techniques, such as capillary electrophoresis and ICP-OES.

So far, there are two main choices to introduce liquid sample into plasma at very low liquid flow rates, after generating an aerosol: (i) those pneumatic micronebulizer coupled to a spray chamber, such as: a high efficiency nebulizer (HEN) [9, 10], a microconcentric nebulizer (MCN) [11–13], a Micromist nebulizer (MMN) [14, 15], a Torch integrated sample introduction system (TISIS) [16, 17] and a dual micronebulizer system [18]) and (ii) the so-called direct injection micronebulizers, direct injection nebulizer (DIN) [19, 20], direct injection high efficiency nebulizer (DIHEN) [21, 22] and Vulkan direct injection nebulizer (Vulkan DIN) [23, 24]. In these later cases, the aerosol is generated at the plasma base and no spray chamber is required. The direct injection of liquid sample into the plasma currently presents potential benefits compared to conventional nebulizer-spray chamber arrangements: (i) 100% analyte transport efficiency into the plasma; (ii) elimination of spray chamber related interferences and noise; (iii) no solution waste production; (iv) low dead volume ($<10\,\mu\mathrm{L}$), hence reduced memory effects and rapid response times; and (v) low nebulizer gas flow rates ($<0.2\,\mathrm{L\,min^{-1}}$) and solution uptake rates (1–100 $\mu\mathrm{L\,min^{-1}}$). Despite these benefits, the micronebulizers (including the direct injection nebulizers) are expensive, fragile and they present a greater susceptibility to nebulizer clogging compared to conventional devices due to the smaller dimensions for the solution capillary and gas annulus areas. This limitation may completely damage the nebulizer. Additionally, the close proximity of the nebulizer tip to the plasma increases the likelihood of accidental and gradual damage to the direct injection nebulizers. The matrix effects caused by organic as well as inorganic compounds can be more severe for a DIHEN [26, 27] than for a sample introduction system based on the use of a spray chamber. This probably explains why this nebulizer is not widely used for routine analysis despite its advantages. Recently, a demountable DIHEN (d-DIHEN) coupled to ICP-MS [28] and interfaced with different separation techniques has been described [29–31].

To explore devices of sample introduction which allow the analysis of microsamples and that overcome the limitations of the already existing sample introduction systems such as their high cost due to its relatively complex setup is a challenge. These devices and related advances are important in many areas: forensic [32], biological [33], clinical, geological, semiconductor, on-chip technology [34], etc., in which sample size may be limited (lower than 1 mL), expensive or hazardous. Additionally, it would be also interesting, to dispose of a system that allows the use of a replaceable capillary, in order to overcome the well known clogging inconvenient presented with small diameters capillaries used in such systems. In this work, a low cost DIHEN with replaceable capillary has been evaluated in ICP optical emission spectroscopy for direct solution introduction and compared to sample introduction commercial systems with low solution uptake rate, such as the HEN-cyclonic spray chamber arrangement. The demountable DIHEN exhibits potential benefits compared to traditional nebulizer-spray chamber arrangements: 100% analyte transport efficiency into the plasma; elimination of spray chamber related interferences and noise; no solution waste production; low dead volume, hence reduced memory effects and rapid response times; and low nebulizer gas flow rates and solution uptake rates compared to conventional nebulizer-spray chamber arrangements. A similar system [28] has been tested using inductively coupled plasma-mass spectrometry (ICP-MS) and up to the best of our knowledge, there are no studies in optical ICP applied to real samples. The studies were performed in terms of the main analytical figure of merits (i.e., sensitivity, signal stability and limits of detection) for plain water solutions and matrix effects caused by inorganic species in ICP-OES. The utility of this system is explored analyzing three certified materials (bovine liver, rice and wheat flours). The applicability of this design is shown by analyzing micro samples of individual scorpion venom for the metal content present in its metaloenzymes.

## Experimental

### *Instrument*

A Perkin-Elmer Model ICP Optima 3000 radially viewed Ar ICP emission spectrometer and a standard demountable type quartz plasma torch were used throughout. The internal diameter (i.d.) of the alumina injector was 2.0 mm. A Gilson minipulse peristaltic pump was used to feed the nebulizer. High efficiency nebulizer, HEN and a glass cyclonic spray chamber were used. Test solution is delivered to the nebulizers by using narrow-bore Tygon tubing (0.381 mm i.d.) to reduce peristaltic-related noise. All functions of the plasma were computer-controlled. The optimized plasma operating parameters such as RF power (1500 W), outer gas flow rate (12 L min$^{-1}$), intermediate gas flow rate (0.5 L min$^{-1}$) were the same for the demountable direct injection high efficiency nebulizer (demountable DIHEN), and for the high efficiency nebulizer coupled to a conventional cyclonic spray chamber (HEN-Cy). However, nebulizer gas flow rate of 0.4 and 0.8 L min$^{-1}$, viewing height above coil of 3 and 5 mm, and sample uptake rate of 80 and 60 $\mu$L min$^{-1}$ were found for the DIHEN and HEN-Cy respectively. Working wavelengths used were Ba(II) 455.4, Cd(II) 226.5, Mg(I) 285.2, Mg(II) 280.2, Mn(II) 257.6, Sr(II) 407.7, Zn(I) 213.8 and Zn(II) 206.2 nm. They were selected based on their sensitivity and freedom from spectral interferences.

A digital image having some critical dimensions of the DIHEN with replaceable capillary constructed in this work is shown in Fig. 1. The DIHEN with replaceable capillary consists of: a borosilicate glass shell; a capillary electrophoresis column, polyimide coated fused silica capillary (BARE $\mu$SIL-FS, 100 $\mu$m internal diameter (i.d), Agilent Technologies,); and a Polyetheretherketone (PEEK) capillary tubing to support the solution capillary (0.5 mm i.d. × 1.57 mm outer diameter (o.d.). The sample capillary extends through the entire length of the nebulizer. The final segment (approx.

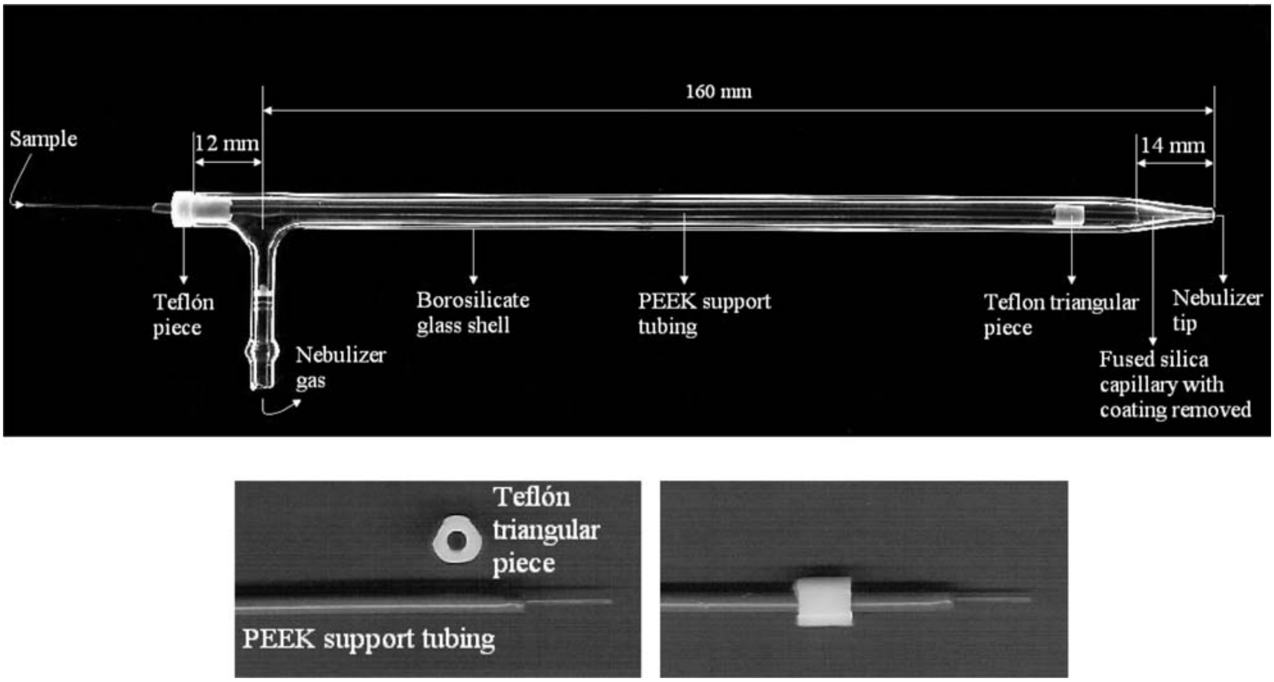

**Fig. 1.** Schematic sketch of the demountable direct injection high efficiency nebulizer

14 mm) of polyimide coating is removed by burning it using an open flame, in order to enhance solution-gas interactions and hence to improve nebulization, otherwise a carbon residue is formed on the nebulizer tip and this perturbs aerosol generation. Two small PTFE pieces with a central orifice serve as support of the PEEK capillary tubing, and also keep the sample capillary align with respect to the nebulizer's tip. The end of the solution capillary is cut using a fused silica capillary cutter (Upchurch Scientific) to ensure a smooth, flush end. Ceramic cutters are not recommended as they often result in an imprecisely cut tip, which in turn produce an asymmetric spray and poor analytical figures of merit. The nebulizer dead volume is ca. 15 µL measured experimentally. The DIHEN with replaceable capillary was placed at 6 mm below the end of the torch inner tube. This position was carefully fixed to shield the tip from the hot zone, avoiding tip melting.

### *Reagents and samples*

ICP multi-element standard solution IV (1000 mg $L^{-1}$) of Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, and Zn was from Merck. All chemicals used were of analytical-reagent grade. Distilled, deionized water (Milli-Q 18 MΩ $cm^{-1}$) was used for solution preparation. Ultra-high-purity commercial acids were used to prepare all reagents, standards and samples.

Standard references NIST 1577b Bovine Liver, NIST 1567 wheat flour, and NIST 1568 rice flour.

Tityus discrepans scorpions kept alive in the laboratory were anaesthetized once a month with $CO_2$ and milked for venom by means of electrical stimulation. The venom was dissolved in deionized water and centrifuged for 15 min. The supernatant was freeze-dried and stored at −80 °C until used.

### *Sample treatment*

The standard reference materials were dissolved according to the following procedure: the dry sample was weighted (0.5000 g) directly into PTFE digestion vessels, previously cleaned, and concentrated nitric acid (5 mL) was added to each vessel and left overnight. Then, heated at 60 °C on a hot plate, for three hours and hydrogen peroxide added (1 mL) and heated for one hour till complete dissolution. After cooling, the digested solutions were transferred into 25 mL volumetric flasks and diluted to volume with distilled deionized water. The final concentration of nitric acid was 10% v/v. A blank was also prepared in the same way. The scorpions' venom samples were analyzed after reconstitution of the lyophilized samples with 150 µL of deionized water.

## Results and discussion

### *Effects of operating conditions with the DIHEN with replaceable capillary*

Plots of signal to noise ratio and robustness (MgII/MgI ratio) are shown in Fig. 2 as a function of nebulizer gas flow rate, observation height and sample aspiration rate using the DIHEN with replaceable capillary. A power of 1500 W was fixed and used through, according to the literature [21, 22, 24–28, 35, 36]. The optimal position of the DIHEN capillary internal tip was exactly at the same position of that of the external borosilicate glass tube tip (position 0 mm). It was optimized moving the internal capillary tube below and out of the nebulizer tip. Moving the capillary tube backward (from 1 to 2 mm from the nebulizer tip) resulted in plasma flickering. However, moving the capillary tube ca. 1 mm outside the nebulizer tip, a good aerosol was obtained with the drawback that the Relative Standard Deviation (% RSD) was very poor (>5%).

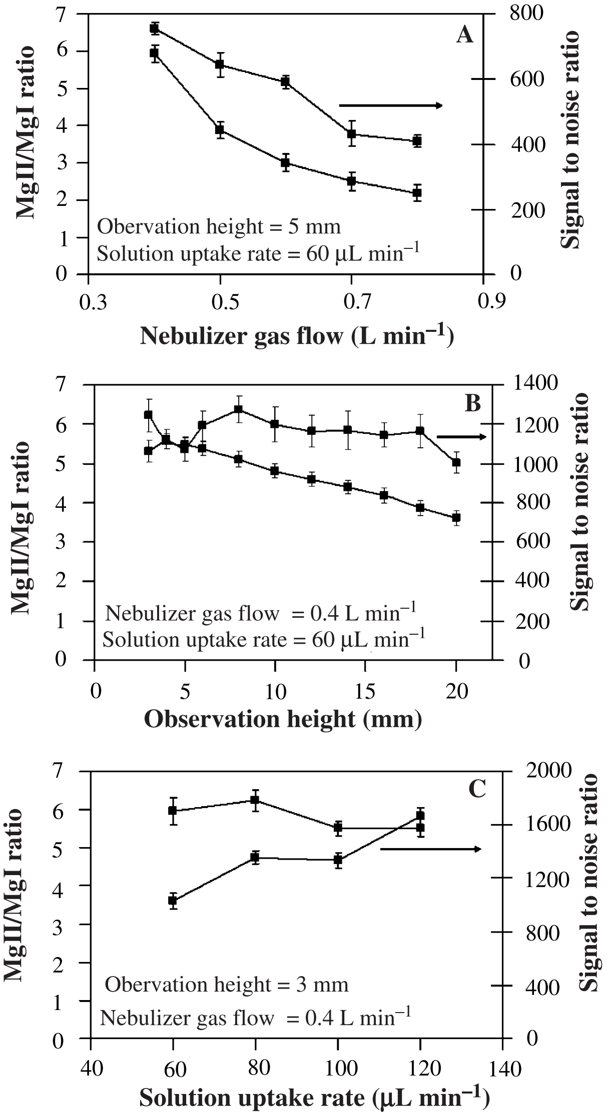

**Fig. 2.** MgII/MgI ratio and signal to noise ratio of MgII as a function of (A) nebulizer gas flow, (B) observation height and (C) solution uptake rate

At nebulizer gas flow rates less than 0.4 L $min^{-1}$, the plasma becomes unstable and begins to flicker due to poor nebulization. At nebulizer glass flow rate greater than 0.4 L min$^{-1}$, signal to noise ratio and MgII/MgI ratio diminished. The optimum nebulizer gas flow rate is 0.4 L min$^{-1}$. This value differs from those obtained by other investigators [21, 22, 24–28, 35, 36] (around 0.12–0.25 L min$^{-1}$). The higher values found in this work may be explained by the PTFE triangular piece that supports the internal capillary which has its three vertices, resting on the inner face of the borosilicate glass shell, and this, in part, obstructs the gas flow pathway. Also, the dimensions of the nebulizer tip can influence the effect observed. Consequently, higher flows are needed in order to have an acceptable nebulization.

The optimum observation height was 3 mm and maximum solution uptake rate was set at 80 µL min$^{-1}$. The optimization criterion was the robustness of the plasma since our objectives are the analysis of samples with complex matrices. The best signal to noise ratio is not necessary obtained under robust conditions. The above conditions differ from those obtained when using the commercial HEN-Cyclonic chamber nebulization system. Optimum conditions for the commercial system were reached, carrying out the same optimization procedure. Both devices are operated at the same RF power, outer and intermediate gas flow rates. However, the nebulizer gas flow rate is lower and the sample uptake rate is higher compared to the HEN-Cyclonic system. The viewing height for the DIHEN with replaceable capillary system was slightly lower.

### *Sensitivity, detection limits and short term stability*

Sensitivity, detection limits (3$\sigma$ of the blank), and short-term precision (% RSD) for the DIHEN with replaceable capillary and HEN-Cy were obtained with a multielement solution of 5 mg L$^{-1}$ and are presented in Table 1 for six elements. Values listed are obtained under optimized conditions for each nebulizer. In general, the DIHEN with replaceable capillary offers better sensitivities than the data provided by the HEN-Cyclonic system. These improvements in sensitivity result in comparable and improved detection limits. The short-term precision was expressed as the relative standard deviation (% RSD) of fluctuations in the emission signal around a mean value from a series of 10 replicates. The precision for the DIHEN with replaceable capillary is not as good as the HEN-Cyclonic system, but being less than 2%, it can still be considered very well acceptable. One of the main advantages of the DIHEN with replaceable capillary over the other system is the improved analytical figures of merit at very low solution uptake rates. The improvements in analytical figures of merit are attributed to the fact that 100% of the sample is introduced into the plasma in direct injection nebulization compared to micronebulizers and reduce-volume spray chambers, such as the HEN-Cyclonic arrangement.

### *Matrix effects caused by nitric acid and sodium*

It has been reported that DIHEN is more susceptible to changes in matrix composition compared to the conventional nebulizer-spray chamber arrangement. The significant solvent load and the higher droplet size distribution into the plasma are the main responsible for this behavior [27, 35]. In this connection, the effect of nitric acid and sodium as NaCl was evaluated separately through the measure of the relative intensi-

**Table 1.** Sensitivity, detection limits, and short-term stability for the demountable DIHEN and HEN-Cy systems

| Element and wavelength/nm | Signal to noise ratio | | Detection limits/ng mL$^{-1}$ | | Precision/% RSD[c] | |
|---|---|---|---|---|---|---|
| | Demountable DIHEN[a] | HEN-Cy[b] | Demountable DIHEN[a] | HEN-Cy[b] | Demountable DIHEN[a] | HEN-Cy[b] |
| Ba 455.403 | 2629 | 1080 | 2.3 | 2.6 | 1.8 | 0.6 |
| Cd 226.502 | 3436 | 3633 | 1.8 | 1.1 | 1.8 | 1.1 |
| Mg 280.270 | 1373 | 549 | 0.5 | 1.9 | 1.7 | 0.6 |
| Mn 257.610 | 1833 | 1722 | 0.9 | 0.6 | 1.9 | 0.3 |
| Sr 407.771 | 3692 | 1942 | 1.1 | 1.0 | 1.8 | 0.4 |
| Zn 206.200 | 1420 | 1213 | 3.8 | 5.4 | 1.7 | 0.5 |
| Zn 213.856 | 4231 | 572 | 2.5 | 3.9 | 1.8 | 1.2 |

[a] Demountable DIHEN: Demountable direct injection high efficiency nebulizer. Sample uptake and nebulization gas flow rate were 80 and 0.4 L min$^{-1}$, respectively.

[b] HEN-Cy: High efficiency nebulizer coupled to a conventional cyclonic spray chambers. Sample uptake and nebulization gas flow rate were 60 and 0.8 L min$^{-1}$, respectively.

[c] Ten replicates analyses of a 5 mg L$^{-1}$ multielement solution.

ty ($I_{rel}$), which is defined as the analytical net emission signal found for solutions of nitric acid (10% v/v) divided by that measured from a plain water solution. Sodium effect (0.1% m/v) was obtained in the same way. Emission lines with low and high excitation energies were used in this experiment. The closer the $I_{rel}$ value to unity, the less severe the matrix effects. Similar to other works [27, 35], significant deviations from unit were obtained with the DIHEN with replaceable capillary due to the presence of nitric acid and sodium chloride matrices. This result may be attributable to the poor plasma robustness conditions reached by the DIHEN with replaceable capillary under the best plasma operating conditions (MgII/MgI was 6.5) compare to than that reached by the spray chamber system (MgII/MgI was 9).

### *Application of DIHEN with replaceable capillary to analysis of reference materials*

The introduction of samples when direct injection nebulizer is used can be problematic due to potentially severe matrix and plasma loading effects. Additionally, nebulizer clogging may also occur due to reduced solution capillary dimensions of microflow nebulizers. In order to test the usability of the DIHEN with replaceable capillary, three standards reference materials eg. Bovine liver, rice flour, and wheat flour were analyzed for seven elements (Ca, Cd, Cu, Fe, Mg, Mn, and Zn). The significance test [37] was applied and no significant differences were found at the 95% confidence level between the results obtained and the certified values. For the individual elements, in each certified material, there was a significant improvement in precision (1–10%) compared to those reported for the certified values for the three reference materials.

### *Analysis of real samples*

Scorpion venom (*Tityus discrepans*) produces profound effects in organs and systems response consisting of hypertension or hypotension, tachycardia, tachypnea, hypothermia, leucocytosis, sialorrhoea, myocarditis, pancreatitis and respiratory distress. Quantification of metal content in animal venoms plays an important role in order to be able to study the catalysis and regulation of proteolytic enzymes which may help to understand the mechanism of action involved in clinical profile resulting from envenomation caused by these venoms.

The ability of the DIHEN with replaceable capillary to analyze micro samples makes it an excellent application for the analysis of metals in several animal secretions such as venoms of snakes, ticks and scorpions, among others. Availability of these samples is very limited.

Individual venom samples were analyzed and the elements Ca, Cd, Cu, Mg, Mn, Sr and Zn were determined. Precisions were lower than 5%. The results shows that this direct injection device can be useful in the analysis of microsamples using ICP-OES.

## Conclusions

A direct injection system (DIHEN) in which the solution capillary is easily replaced in the event of clogging or melting was described. It can be easily constructed in the laboratory and used to analyze very small volumes of samples in ICP-OES. Figures of merit reached with this unit are similar or better than those showed by conventional micro nebulizer-spray chamber arrangement. This device was more susceptible to changes in matrix composition. The accuracy of the method using the DIHEN with replaceable capillary was proven by the analysis of three certified reference materials, showing good accuracy and acceptable precision. The ability of the system to analyze samples is shown by the analysis of metals in venoms of scorpions, whose sample's availability is very limited.

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