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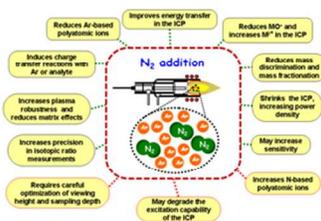
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Graphical Abstract  
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# Advantages, drawbacks and applications of mixed Ar-N<sub>2</sub> sources in inductively coupled plasma-based techniques: an overview

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This review deals with mixed gas Ar-N<sub>2</sub> plasmas, highlighting advantages, limitations and applications of them in inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) techniques, covering publications in the last three decades. Fundamental plasma parameters (such as electron number density, excitation or ionization temperatures, oxides and spatial profiles of ions distribution), performance of the mixed gas Ar-N<sub>2</sub> plasmas, figures of merit are presented and discussed in order to demonstrate the effects of adding N<sub>2</sub> to the Ar-ICP.

## 1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP OES) have been widely used for elemental or isotopic analysis over the last decades. However, non-spectroscopic interferences (also known as matrix effects), operating costs, insufficient energy for effective ionization of certain elements (such as halogens, S and P), interferences by polyatomic ions in ICP-MS, and limitations for samples with organic solvents and/or carbon have been found.<sup>1-6</sup> These drawbacks have stimulated research for partial or total replacement of Ar by other gases (atomic or molecular), producing the so-called mixed-gas plasmas.<sup>9-11</sup>

Mixed Ar-N<sub>2</sub> plasmas are obtained when one of the three main flows of Ar (principal, auxiliary or nebulizer) is partially or totally replaced, or when N<sub>2</sub> is just added to them. The higher thermal conductivity of N<sub>2</sub> causes better heat transfer in the ICP, which results in better energy coupling between the induction zone and the central channel of the ICP. Therefore, the addition of N<sub>2</sub> may affect several processes occurring in the ICP. As a consequence, several interferences by polyatomic ions in ICP-MS and non-spectroscopic interferences in both ICP-MS and ICP OES can be mitigated, which extends the application for more complex matrices, an important advantage for these techniques. Nitrogen can be handled safely and well tolerated by conventional ICP OES and ICP-MS instruments when compared to other mixed-gas plasmas such as Ar-He or Ar-O<sub>2</sub> and Ar-H<sub>2</sub>. Thus, mixed gas Ar-N<sub>2</sub> plasmas have more potential for applications, solving specific spectroscopic or non-spectroscopic interferences.

Review articles about mixed-gas plasmas were published - by Montaser and Van Hoven,<sup>9</sup> encompassing only atomic emission spectrometry, in 1987, and by Durrant<sup>11</sup>, emphasizing ICP-MS,

in 1993. The theme was also reviewed and discussed in books published by Montaser and Golightly, in 1992,<sup>4</sup> and Beauchemin et al., in 2000.<sup>5</sup> Since then, instrumentation has undergone various changes but new review articles on this field have not been published. The present review is about mixed-gas Ar-N<sub>2</sub> plasmas exclusively, with the aim to highlight the effects of N<sub>2</sub> addition to the Ar-ICP. Studies and applications using ICP-based techniques (ICP OES, ICP-MS and LA-ICP-MS) published in the last three decades are presented.

## 2. General and fundamental aspects of mixed Ar-N<sub>2</sub> plasmas

The N<sub>2</sub>-Ar-ICP moves closer to the state of local thermodynamic equilibrium (LTE) as the concentrations of N<sub>2</sub> in the plasma gas is increased; the LTE model predicts that the N<sub>2</sub>-Ar-ICP has maximum temperatures (9900 - 10100 K) comparable to that of Ar-ICP (10600 K).<sup>9-11</sup> However, the predicted temperature is reduced as the concentration of N<sub>2</sub> is increased.<sup>12</sup> Increasing of thermal conductivity in the ICP is expected with N<sub>2</sub> addition, since N<sub>2</sub> has a thermal inductivity 32 times that of Ar at 7000 K.<sup>13</sup>

Addition of N<sub>2</sub> to the outer gas may decrease the excitation temperature and cause excess of cooling due to high thermal conductivity.<sup>9</sup> Addition of N<sub>2</sub> to the auxiliary gas is not common because unstable plasmas are usually obtained. Thus, N<sub>2</sub> has mostly been added to the nebulizer gas and introduced in the central channel of the Ar-ICP.<sup>1</sup> Addition of N<sub>2</sub> to the nebulizer gas tends to cause a widening of the central channel through the ICP, an effect that tends to reduce the sensitivity in ICP-MS whereas addition to the outer gas causes an overall constriction of the entire plasma.<sup>15</sup> In any case, whenever Ar is completely replaced in one or more Ar flows, care should be taken to watch for a secondary discharge

1 in non-adequately grounded ICP-MS instruments, which  
2 invalidate spatial profiling of ions signal, an useful tool for  
3 fundamental studies.<sup>14</sup>

4 Nitrogen is a diatomic gas with vibrational modes and is  
5 capable of storing energy. Argon, which is monatomic, has  
6 lower heat and electrical capacity than N<sub>2</sub>. As a consequence, a  
7 greater applied power is necessary for maintenance and  
8 operation of a N<sub>2</sub>-Ar-ICP, which increases instrument cost.<sup>1-3</sup>  
9 Thus, instrumentation for mixed-gas plasmas has been  
10 considered impractical and non-competitive with that for  
11 standard Ar-ICP.

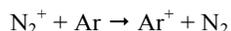
12 Depending on the amount of N<sub>2</sub> added and addition mode,  
13 different mixed plasmas can be obtained and the observation  
14 height for laterally-viewed plasma (in ICP OES), sampling  
15 depth (in ICP-MS), applied power, and gases flow rate must be  
16 optimized for each composition of the mixed plasma. If the  
17 optimization is not followed, appropriate comparisons of results  
18 obtained by using N<sub>2</sub>-Ar-ICP and Ar-ICP may end up invalid or  
19 impossible. In some cases, a multivariate approach has been  
20 used for optimization.<sup>12,16</sup>

21 Sesi et al.<sup>17</sup> observed that N<sub>2</sub> addition to the nebulizer gas  
22 flow cools the center channel of the plasma. They proposed that,  
23 as a molecular gas, the vibrational and rotational states of N<sub>2</sub>  
24 dissipate heat transferred into the center of the ICP. However,  
25 when N<sub>2</sub> was added to the auxiliary gas flow, an increase in the  
26 temperature of the central channel was observed. They  
27 attributed this effect to N<sub>2</sub>, which improves transfer of energy  
28 from the outer gas flow to the center channel of the plasma.  
29 Comparison of ion signal lateral profiles collected by Agatomor  
30 and Beauchemin<sup>18</sup> from an Ar-ICP and N<sub>2</sub>-Ar-ICP revealed the  
31 plasma shrinks when N<sub>2</sub> is introduced in the outer gas plasma.  
32 The different physical properties between N<sub>2</sub> and Ar causes this  
33 plasma phenomena (volume reduction), known as thermal  
34 pinch or plasma shrinks. The plasma shrinkage moves the IRZ  
35 (initial radiation zone) away from the sampling cone, thereby  
36 requiring an increase in nebulizer carrier gas flow rate or a  
37 lower sampling depth (in ICP-MS) and optimization of the  
38 observation height (in laterally-viewed ICP OES).<sup>9-11</sup>

39 Chemical elements can be ionized in different ways in the  
40 Ar-ICP, mainly by thermal ionization, Penning ionization, or  
41 ionization by charge transfer. The thermal ionization involves  
42 collisions with energy exchange between atoms, ions or  
43 electrons, the Penning ionization does between atoms in the  
44 ground state and metastable Ar species, while ionization by  
45 charge transfer involves charge exchange between neutral and  
46 ionized species. The foreign gas (N<sub>2</sub>) added can induce shifts of  
47 the thermodynamic equilibrium of the ICP, favouring either  
48 process.<sup>1,9</sup>

49 Comparison of the analyte profiles with those of  
50 background ions suggested that electron-impact ionization is  
51 the predominant ionization mechanism in the Ar-ICP whereas  
52 charge-transfer with Ar<sup>+</sup> in the N<sub>2</sub>-Ar-ICP was suggested by the  
53 close match of the Ar dimer ion profile and those of the  
54 analytes<sup>19</sup>

55 Houk et al.<sup>10</sup> observed migration of N<sub>2</sub><sup>+</sup> species into the  
56 central channel of the ICP when N<sub>2</sub> was added to the outer gas.  
57 The authors also cited that Ar<sup>+</sup> and Ar<sup>2+</sup> can be produced in  
58 different regions of the ICP, being Ar<sup>+</sup> present predominantly in  
59 the central channel and Ar<sup>2+</sup> in the induction region. When the  
60 outer gas used (Ar) was completely replaced by N<sub>2</sub>, the  
presence of Ar<sup>+</sup> in the central channel of the ICP was still  
detected. The authors then suggested the following charge  
transfer reaction:



The ionization potential of N<sub>2</sub> (15.58 eV) is close to that of  
Ar (15.76 eV) and the occurrence of charge transfer reaction  
among N<sub>2</sub> and Ar in the N<sub>2</sub>-Ar-ICP is possible. The similar spin  
configurations of both species should also be considered.<sup>18</sup> The  
N<sub>2</sub><sup>+</sup> and N<sup>+</sup> species produced may react with oxygen present in  
the plasma and give rise to NO<sup>+</sup> (ionization potential of 9.26  
eV), a species which can also increase the ionization of the  
analyte by charge transfer. The formation NO<sup>+</sup> (strongly  
bonded, D<sub>0</sub> = 11.76 eV) would also effectively sequester O  
atoms present in the ICP and prevent the formation of MO<sup>+</sup>  
species from analyte ions.

Spatial signal profiles of analytes in different regions of an  
N<sub>2</sub>-Ar-ICP revealed that analytes with low ionization potential  
(IP) had similar radial profiles to that of NO, while only a small  
central peak could be observed for analytes with higher IP than  
NO, suggesting a charge-transfer ionization mechanism  
between NO and analyte.<sup>13</sup>

## 2.1. Use of mixed Ar-N<sub>2</sub> plasmas in ICP OES

Addition of N<sub>2</sub> to the Ar-ICP has been early investigated in  
order to improve the sensitivity for the laterally-viewed ICP  
and reduce costs due to Ar consumption. Montaser and co-  
workers.<sup>13,21</sup> compared the performance of both Ar-ICP and N<sub>2</sub>-  
Ar-ICP and observed that the analyte and the background  
signals increased in the same order without improvement of the  
limit of detection (LOD). These researchers also noted that the  
noise increased when N<sub>2</sub> was added to the outer plasma gas,  
restricting the analytical application of the N<sub>2</sub>-Ar-ICP for  
various emission lines between 200 and 300 nm, due to  
emission of molecular nitrogen species.<sup>9,21</sup> In these studies,  
increasing amount of N<sub>2</sub> was added to the outer gas flow or  
nebulizer gas flow until complete replacement of Ar by N<sub>2</sub>.

Few studies have focused addition of N<sub>2</sub> to the Ar-ICP  
axially-viewed.<sup>22-24</sup> In the work conducted by Ohata et al.<sup>20</sup>, N<sub>2</sub>  
at flow rate of 1 L min<sup>-1</sup> was added to the outer gas, being  
pneumatic nebulization (PN) used for introducing the solution  
in the ICP. By comparing both Ar-ICP and N<sub>2</sub>-Ar-ICP, the  
limits of detection (LODs) of atomic lines were similar or  
higher in N<sub>2</sub>-Ar-ICP while those of ionic lines were lower in  
the N<sub>2</sub>-Ar-ICP. The authors have also observed the ratio Mg(II)  
280 nm/Mg(I) 285 nm emission intensities increased from 7 to  
20 but became constant at 0.2 L min<sup>-1</sup> or higher N<sub>2</sub> flow rate. In  
a study conducted more recently,<sup>23</sup> a low flow of N<sub>2</sub> (flow rate  
of 20 mL min<sup>-1</sup>) was added to the central channel of the ICP,  
through the nebulizer gas. The ratio Mg(II)280.270  
nm/Mg(I)285.213 nm, utilized as diagnostic for plasma  
robustness, increased from 14 to 20 for PN, and 12 to 25 for  
pneumatic nebulization with aerosol desolvation (PN-DES).  
For 40 emission lines evaluated, it was observed that the  
intensity of most of them increased under addition of N<sub>2</sub> to the  
nebulizer gas (see Figure 1). Detection limits, precision, and  
linearity of calibration curves obtained by using N<sub>2</sub>-Ar-ICP  
were almost similar to those obtained by using Ar-ICP. The  
slope of calibration curves (sensitivity) was generally improved  
by N<sub>2</sub> addition but the LODs remained almost the same. The  
main reason was that N<sub>2</sub> not only enhanced the analyte signal  
but also the background. However, matrix effects (caused by  
Na, K and Ca) were mitigated by adding the low flow of N<sub>2</sub>  
while precision and accuracy were not deteriorated.

With respect to applications using N<sub>2</sub>-Ar-ICP, it was found  
that the addition of a small flow of N<sub>2</sub> (20 mL mi<sup>-1</sup>) in the  
nebulizer gas allowed direct analysis of rice slurry, which was  
introduced into the N<sub>2</sub>-Ar-ICP through PN.<sup>24</sup> To this end, Y(II)

(371.029 nm) was used as internal standard; the relative standard deviation (RSD) was typically lower than 10% and accuracy close to 100%. Vaporization of major elements in slurries of metals, metal oxides, metal carbides and coals were in general improved by adding N<sub>2</sub> (10%) to the outer gas.<sup>16</sup> However, the plasma volume and sensitivity were reduced.

The addition of N<sub>2</sub> alters fundamental plasma parameters, however charge transfer reactions between species produced in the ICP (N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, NO<sup>+</sup>, NH<sup>+</sup>, ArN<sup>+</sup>) and the analyte cannot be excluded.<sup>50</sup> An increase of the signal of an emission line with energy similar of that of the gas added is an indication that it promotes charge transfer reactions. However, the identification of this mode of excitation is difficult, mainly because of masking of excitation and collision processes. The effect of N<sub>2</sub> on the electron density, electron temperature, gas kinetic temperature on Ca(II) emission were investigated by Sesi and co-workers.<sup>17</sup> They observed that the addition of N<sub>2</sub> to the central channel of the Ar-ICP decreased the electron density and electron temperature.

Addition of N<sub>2</sub> to the outer gas of an Ar-ICP has a completely different effect than adding it to the central channel gas. The former increases power density and improves plasma robustness (at the expense of sensitivity) whereas the latter cools down the central channel,<sup>17,25</sup> thus decreasing plasma robustness. However, as N<sub>2</sub> possess higher thermal conductivity than Ar, it usually increases energy transfer among the bulk plasma and the central channel when present as a sheathing gas in the central channel. The net effect is dependent on the amount of N<sub>2</sub> added to the Ar-ICP. For example, it has been observed<sup>23,32</sup> the plasma robustness (following the Mg(II)280.270 nm/Mg(I)285.213 nm criterion) was increased by adding a small flow of N<sub>2</sub> (up to 20 or 40 mL min<sup>-1</sup>) in the central channel of the Ar-ICP. The exact mechanism of action of N<sub>2</sub> in the Ar-ICP is unknown with respect to the reduction of matrix effects in ICP OES. Nitrogen may decrease the plasma electron density in certain regions and, consequently, change the energy distribution in the ICP. Since the electron density decreases, the excitation by electron impact can be reduced, making matrix effects less severe. Besides, electronic equilibrium shifts must also be considered. Another possibility is the decrease of the volume of the central channel of the ICP, thus increasing the applied power density, which results in higher power for excitation and or ionization.

**Table 2**

**Fig. 1**

## 2.2 Use of mixed Ar-N<sub>2</sub> plasmas in ICP-MS

Despite the many advantages of ICP-MS such as a high sample throughput, multi-elemental feature, high sensitivity and very good precision, it is subject to many spectroscopic (by polyatomic ions) and non-spectroscopic interference. The polyatomic ions originate from water, acid and other reagents, matrix constituents, Ar and gases from the atmosphere. While spectroscopic interferences have their origin in background and matrix-induced polyatomic and isobaric ions, matrix effects can originate in the sample introduction system, within the plasma, during the extraction of ions through the sampler and skimmer cones, and during transport of ions through the ion optics. This makes the elimination/correction of matrix effects more difficult than that of spectroscopic interference. Instrumental

developments such as double-focusing sector-field ICP-MS with resolution up to 10,000, and collision/reaction cells to chemically resolve the interfering polyatomic ions have been made to eliminate spectroscopic interferences.

The use of mixed-gas plasmas can be useful for reducing interferences in ICP-MS. Addition of N<sub>2</sub> has been made for that purpose, not only to reduce the formation of interfering polyatomic species, but also matrix effects. A more robust plasma is achieved by addition of N<sub>2</sub> to the outer gas,<sup>23</sup> which may improve sample desolvation, vaporization, atomization, and ionization.

Despite the advantages of adding N<sub>2</sub> to the Ar-ICP, it can give rise to interfering polyatomic nitrogen species, as those cited in Table 1. The polyatomic ions generation will depend on the amount of N<sub>2</sub> added, the probability of formation of these ions (diatomic species are more likely than triatomic species), and sample matrix.

**Table 1** Potential interferences by polyatomic nitrogen ions in ICP-MS

Isotope	Polyatomic Ions
<sup>28</sup> Si	<sup>14</sup> N <sup>14</sup> N <sup>+</sup>
<sup>29</sup> Si	<sup>14</sup> N <sup>14</sup> NH <sup>+</sup> , <sup>14</sup> N <sup>15</sup> N <sup>+</sup>
<sup>30</sup> Si	<sup>14</sup> N <sup>16</sup> O <sup>+</sup>
<sup>31</sup> P	<sup>15</sup> N <sup>16</sup> O <sup>+</sup> , <sup>14</sup> N <sup>16</sup> OH <sup>+</sup> , <sup>15</sup> N <sup>15</sup> NH <sup>+</sup>
<sup>42</sup> Ca	<sup>14</sup> N <sup>14</sup> N <sup>14</sup> N <sup>+</sup> , <sup>12</sup> C <sup>14</sup> N <sup>14</sup> O <sup>+</sup>
<sup>46</sup> Ti, <sup>46</sup> Ca	<sup>14</sup> N <sup>16</sup> O <sup>16</sup> O <sup>+</sup> , <sup>32</sup> S <sup>14</sup> N <sup>+</sup>
<sup>49</sup> Ti	<sup>35</sup> Cl <sup>14</sup> N <sup>+</sup>
<sup>50</sup> Ti, <sup>50</sup> Cr, <sup>50</sup> V	<sup>36</sup> Ar <sup>14</sup> N <sup>+</sup> , <sup>35</sup> Cl <sup>15</sup> N <sup>+</sup>
<sup>51</sup> V	<sup>36</sup> Ar <sup>15</sup> N <sup>+</sup> , <sup>36</sup> Ar <sup>14</sup> NH <sup>+</sup> , <sup>37</sup> Cl <sup>14</sup> N <sup>+</sup>
<sup>52</sup> Cr	<sup>38</sup> Ar <sup>14</sup> N <sup>+</sup> , <sup>36</sup> Ar <sup>15</sup> NH <sup>+</sup>
<sup>54</sup> Fe, <sup>54</sup> Cr	<sup>40</sup> Ar <sup>14</sup> N <sup>+</sup> , <sup>38</sup> Ar <sup>15</sup> N <sup>+</sup>
<sup>55</sup> Mn	<sup>40</sup> Ar <sup>15</sup> N <sup>+</sup> , <sup>40</sup> Ar <sup>14</sup> NH <sup>+</sup>
<sup>56</sup> Fe	<sup>40</sup> Ar <sup>15</sup> NH <sup>+</sup>
<sup>64</sup> Zn	<sup>36</sup> Ar <sup>14</sup> N <sub>2</sub> <sup>+</sup>
<sup>68</sup> Zn	<sup>40</sup> Ar <sup>14</sup> N <sub>2</sub> <sup>+</sup>
<sup>70</sup> Ge, <sup>70</sup> Zn	<sup>40</sup> Ar <sup>14</sup> N <sup>16</sup> O <sup>+</sup>

## 2.2.1 Investigations concerning mixed Ar-N<sub>2</sub> plasmas in ICP-MS

### 2.2.1.1 N<sub>2</sub> added to the outer gas

Lam and Horlick<sup>34</sup> reported the analyte (Zn, Ge, As, Sr, Y, Zr, Ru, Te, Cs, Ba and Ce) signal increased 4 times while oxides (MO<sup>+</sup>) and polyatomic background ions (ArO<sup>+</sup>, ArOH<sup>+</sup>, Ar<sup>+</sup> and ClO<sup>+</sup>) decreased under 5% N<sub>2</sub> in the outer gas. By using the same flow of N<sub>2</sub>, Beauchemin and Craig<sup>44</sup> reported that the effect of 0.01 mol L<sup>-1</sup> Na on <sup>56</sup>Fe, <sup>57</sup>Fe, <sup>76</sup>Se, <sup>78</sup>Se was overcome whereas precision and accuracy of <sup>57</sup>Fe/<sup>56</sup>Fe<sup>+</sup> and <sup>76</sup>Se<sup>+</sup>/<sup>78</sup>Se<sup>+</sup> ratios were improved. The sensitivity was reduced up to 5 but the stability of the ICP was better, resulting in similar (for Se) or better (for Fe) LODs. For 2-10% of N<sub>2</sub>, the LODs for Cr, Fe, and Se were improved while mass discrimination and matrix (0.01 mol L<sup>-1</sup> K) effect were eliminated. The same authors<sup>52</sup> have also investigated the effect of K (up to 0.1 mol L<sup>-1</sup>) on Al, V, Cr, Fe, Co, Ni, Cu, Zn, Se, Cd and Pb under 2-10% N<sub>2</sub> in the outer gas. Sensitivity decreased upon addition of N<sub>2</sub> along with the signal-to-noise (S/N) and signal-to-background (S/B) ratios, except for those analytes suffering interferences from Ar polyatomic species (Cr, Fe and Se) where N<sub>2</sub> then improved S/N and S/B. The decrease in sensitivity was smaller for Cd, Zn and Se, as N<sub>2</sub> probably improved the ionization of these elements (which are

not 100% ionized in an argon plasma). Mass discrimination was reduced in the  $m/z$  range 51-78. The effect of  $0.01 \text{ mol L}^{-1} \text{ K}$  in the  $m/z$  range 51-114 was eliminated with 10%  $\text{N}_2$  in the outer gas. According to Holliday and Beauchemin,<sup>19</sup> the  $\text{N}_2$ -Ar-ICP (5.9%  $\text{N}_2$  in the outer gas) revealed to be more robust than the Ar-ICP. Matrix-induced enhancement effect was greatly reduced and oxide formation decreased by an order of magnitude, but sensitivity was worsened. The spatial distribution profile of ions in the ICP suggested that electron impact is the predominant mechanism in Ar-ICP. In  $\text{N}_2$ -Ar-ICP, a similar profile of signals of  $\text{Ar}^{2+}$  and analytes suggested charge transfer as the predominant mechanism; the ion transferring charge could be  $\text{NO}^+$ , or  $\text{N}^+$  or  $\text{Ar}^+$ , which originated in the induction region and migrated towards the central channel. Agatemor and Beauchemin<sup>18</sup> conducted a multivariate optimization for maximum sensitivity in an attempt to find conditions for minimizing matrix effects without sacrificing the LODs. At optimized conditions they observed that the analyte (Al, Be, Bi, Co, Ir, Li, Mo, Pb, Pd, Pt, Rh, Ru, Th, Tl, U, V) signal suppression in presence of  $0.1 \text{ mol L}^{-1} \text{ Na}$  was significantly higher in Ar-ICP than in the mixed-gas plasma with 0.13%  $\text{N}_2$  in the outer gas and 0.11% in the central channel where  $\text{N}_2$  was added as a sheath gas around the nebulizer gas flow. Adding  $\text{N}_2$  to both the outer gas and the central channel significantly increased plasma robustness. Such mixed-gas plasma was more efficient at reducing matrix effects. Better LODs were observed for Al, Co, Pd, and V with the optimized mixed-gas plasma compared to argon plasma at maximum sensitivity. Radial profiles obtained for Pt suggested better energy transfer between the toroidal zone and the central channel in the  $\text{N}_2$ -Ar-ICP.

### 2.2.1.2 $\text{N}_2$ added to the nebulizer gas

A study conducted by Evans and Ebdon<sup>41</sup> revealed the production of  $\text{ArCl}^+$ ,  $\text{ArO}^+$ ,  $\text{Ar}_2^+$  and  $\text{Cl}_2^+$  in the ICP was reduced under  $30 \text{ mL min}^{-1}$  of  $\text{N}_2$  in the nebulizer gas. According to Newman and colleagues,<sup>43</sup> formation of  $\text{NdO}^+$  in the supersonic expansion was depressed and precision of isotope ratio measurements ( $^{144}\text{Nd}/^{147}\text{Nd}$ ) improved for a  $\text{N}_2$  flow rate up to  $5 \text{ mL min}^{-1}$  in the nebulizer gas. As observed by Velde-Koerts and Boer,<sup>46</sup> interference by polyatomic ions (on  $^{51}\text{V}$ ,  $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$ ,  $^{58}\text{Ni}$ ,  $^{60}\text{Ni}$ ,  $^{63}\text{Cu}$ ,  $^{65}\text{Cu}$ ,  $^{66}\text{Zn}$ ,  $^{68}\text{Zn}$ ,  $^{75}\text{As}$ , and  $^{82}\text{Se}$  in presence of  $0.02 \text{ mol L}^{-1} \text{ Na}$  or  $\text{Cl}$ ,  $0.01 \text{ mol L}^{-1} \text{ Ca}$  or  $\text{Mg}$ , and  $0.004 \text{ mol L}^{-1} \text{ SO}_4^{2-}$ ) and matrix-induced sensitivity changes were properly reduced at  $\text{N}_2$  flow rate of  $10 \text{ mL min}^{-1}$ , whereas the  $\text{BaO}^+/\text{Ba}^+$  ratio and  $\text{Ba}^{+2}$  signal increased at  $\text{N}_2$  flow rate up to  $20 \text{ mL min}^{-1}$ . Holliday and Beauchemin<sup>50</sup> investigated distribution of ions in cold Ar-ICP and in  $\text{N}_2$ -Ar-ICP ( $\text{N}_2$  flow rate ranging from 60 to  $120 \text{ mL min}^{-1}$  in the nebulizer gas) in presence and absence of  $0.1 \text{ mol L}^{-1}$  or  $0.01 \text{ mol L}^{-1} \text{ Na}$ . The authors observed the central channel in both plasmas was similar and  $\text{NO}^+$  abundant in Ar- $\text{N}_2$ -ICP, a species responsible for charge transfer reactions.<sup>19</sup> According to Craig and Beauchemin,<sup>51</sup> interference by  $\text{Ar}_2^+$  and  $\text{ArCl}^+$  on  $^{75}\text{As}^+$  and  $^{78}\text{Se}^+$  was reduced in presence of  $30 \text{ mL min}^{-1} \text{ N}_2$  in the nebulizer gas.<sup>51</sup> Ford and colleagues,<sup>55</sup> by multivariate optimization of RF power, potential of ion lenses and nebulizer gas flow rate, concluded that the addition of  $\text{N}_2$  (up to 8% in the nebulizer gas) did not improve the signal-to-noise ratio and LODs for  $^7\text{Li}$ ,  $^9\text{Be}$ ,  $^{59}\text{Co}$ ,  $^{85}\text{Rb}$ ,  $^{115}\text{In}$ ,  $^{130}\text{Te}$ ,  $^{159}\text{Tb}$ ,  $^{197}\text{Au}$ ,  $^{209}\text{Bi}$ , and  $^{238}\text{U}$ . On the other hand, Durrant<sup>56</sup> observed that the intensity for several isotopes (from  $^7\text{Li}$  to  $^{209}\text{Bi}$ ) was enhanced while the  $\text{Ba}^{2+}$ ,  $\text{Ce}^{2+}$ ,  $\text{BaO}^+$ ,  $\text{CeO}^+$ ,  $\text{MoO}^+$ ,  $\text{TiO}^+$ ,  $\text{WO}^+$  and  $\text{ZrO}^+$  levels were maintained below 3% of their singly charged ions ( $\text{M}^+$ ) under  $35 \text{ mL min}^{-1} \text{ N}_2$  in the nebulizer gas. Interferences from polyatomic species of nitrogen

and no significant increase in background signals were observed. In general, the signal-to-background ratio was increased.

Applications of mixed gas Ar- $\text{N}_2$  plasmas, where  $\text{N}_2$  was introduced into the ICP through the outer gas (plasma gas), nebulizer gas or intermediate gas, for element determination using ICP-MS are summarized in Table 3.

**Table 3**

It can be observed in Tables 2 and 3 that, in general, the main advantages of the addition of  $\text{N}_2$  include: increased sensitivity, plasma robustness, precision and accuracy; greater tolerance to complex matrices; and, in the case of ICP-MS, reduction of mass bias, polyatomic ions and oxides. In some cases, degradation of sensitivity and LODs are reported, but most studies demonstrate that the addition of  $\text{N}_2$  is beneficial. According to Tables 2 and 3, the beneficial effects observed seem to be independent on the mode of addition of  $\text{N}_2$ . However, when introduced in the central channel of the ICP through the nebulizer gas, a much smaller amount of  $\text{N}_2$  is necessary for producing beneficial effects.

According to Lam and McLaren<sup>15</sup>, the beneficial effect of the addition of  $\text{N}_2$  to the outer gas is enhanced by combination with reduction of the water loading. Several authors report the use of a micronebuliser associated with a desolvation membrane and a low flow of  $\text{N}_2$  ( $10$  to  $15 \text{ mL min}^{-1}$ ).<sup>57-67</sup> After desolvation, the nebulizer gas is mixed with the small flow of  $\text{N}_2$ , for assisting in sample transport and reduction of oxide production in the plasma.<sup>64</sup> The main benefits observed in several applications were reduction of oxides and polyatomic ions, and better precision in isotope ratio measurements. Nevertheless, the effect of  $\text{N}_2$  alone has not been systematically evaluated in most of these applications methods.<sup>59-67</sup>

### 3 LA-ICP-MS

The use of laser ablation (LA) associated with ICP-MS has grown substantially on the last decade. It combines the conveniences of solid sampling with the high sensitivity of ICP-MS.<sup>1-3</sup> However, the need of matrix-matched standards for calibration and fractionation effect (different vaporization for different isotopes) still deprive the use of LA-ICP-MS in routine quantitative analysis.

Addition of a molecular gas to the Ar-ICP may be beneficial for analytical purposes in PN-ICP-MS. Advantages, particularly an increase in sensitivity and a reduction in oxide levels, can also be obtained in LA-ICP-MS. However, the relatively low water loading of the ICP may influence its thermodynamic properties such that one analytical improvement would be different of those obtained with PN-ICP-MS.

Energy transfer from gas to ablated sample particles within the axial channel of the ICP can be better with a small dose of  $\text{N}_2$  in the Ar carrier gas flow. As previously mentioned, the location of the addition of the foreign gas may affect processes in the ICP.<sup>15</sup> Addition of  $\text{N}_2$  to the aerosol carrier gas flow results in a plasma resembling cold Ar-ICP,<sup>50</sup> with a wider and more diffuse central channel than that found under normal operating conditions of an Ar-ICP. However, the  $\text{N}_2$ -Ar-ICP is able to vaporize elements to a greater degree than the cold plasma.

Studies and applications dealing with the use of  $\text{N}_2$  in LA-ICP-MS are listed in Table 4 where it can be seen that the addition of small flow of  $\text{N}_2$  increases the sensitivity and accuracy for various isotopes, decreases interference by oxides and hydrides and decreases mass bias.

Table 4

#### 4. Conclusions and perspectives

Addition of N<sub>2</sub> to the Ar-ICP modifies the energy transfer occurring in the ICP, significantly increasing the robustness thereof. To obtain best results with mixed-gas plasmas, the main parameters should be adjusted/optimized to the new plasma generated. Most studies have shown that the introduction of N<sub>2</sub> to Ar-ICP is useful for reducing spectroscopic and non-spectroscopic interferences. In numerous applications it is noted that small amounts N<sub>2</sub> added to the outer gas may alleviate interferences by polyatomic ions and oxides in ICP-MS, allowing alternative calibration strategies such as isotopic dilution or the monitoring of unusual isotopes with improved LODs in comparison with those for standard Ar-ICP. This calls for additional and systematic applications for specific samples and analytes. A clear disadvantage of the Ar-N<sub>2</sub> plasmas is the increase of nitrogen-based polyatomic species in ICP-MS or structured background originated by diatomic nitrogen molecules in ICP OES that is not extensively discussed in the literature. However, the magnitude of these interferences relies on the amount of N<sub>2</sub> added to the Ar-ICP. Further studies about addition of N<sub>2</sub> to the Ar-ICP are needed, using low flow of N<sub>2</sub>, with newer and more sensitive instrumentation, mainly in the case of ICP OES. There have been few studies about the use of N<sub>2</sub> in ICP OES where, in general, large amount of the gas has been added to the Ar-ICP. This approach lies on the amount that an rf generator designed to operate with Ar can tolerate N<sub>2</sub>. However, benefits of N<sub>2</sub> takes place with the use of small amounts of the gas in both ICP OES and ICP-MS techniques.

Care must be taken when comparing results of different studies owing the use of distinct instruments or even gas composition (volumetric fraction) and way of addition, which may produce inconsistent data. It was possible to gauge from the articles reported that N<sub>2</sub> acts more effectively when added in the nebulizer gas (in the central channel of the ICP) rather than in the outer gas plasma. The main reason is the secondary discharge present in several instruments, which has prevented the generation of stable mixed Ar-N<sub>2</sub> plasmas. Therefore, addition of lower amount of N<sub>2</sub> has preferentially been carried out, which can be more effective in the central channel of the ICP. In this case, N<sub>2</sub> does not reach directly the induction region of the ICP and less energy is spent in the bulk plasma (for N<sub>2</sub> vibration and dissociation). Thereby, small amounts of this foreign gas in the central channel increases the energy coupling efficiency, with a little (or none) degradation on the plasma excitation capability.

Fundamental studies including axially/laterally spatial profiles of ions and emission species are required for plasma diagnostics, not only to compute significant changes on plasma characteristics but, also to indicate additional excitation and ionization mechanisms taking place in the Ar-N<sub>2</sub> plasmas. Finally, use of N<sub>2</sub> combined with different sample introduction systems (high efficiency and miniaturized nebulizers, ultrasonic nebulizers, pneumatic nebulizers associated with aerosol desolvation systems, electrothermal vaporization, and laser ablation) still remain a topic of study mainly to upgrade plasma characteristics in comparison with conventional PN.

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#### Notes and references

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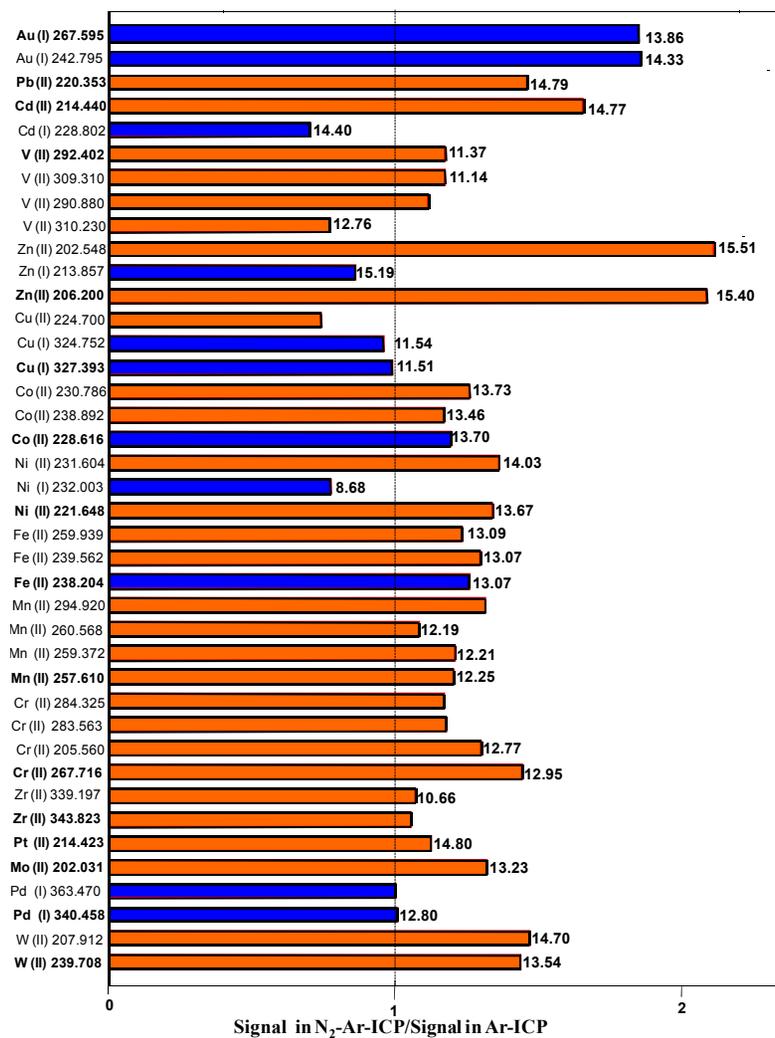
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**Fig. 1** Signal enhancement or reduction of the atomic (I) and ionic (II) emission lines resulting from the addition of N<sub>2</sub> to the nebulizer gas. The numbers inside the figure are the energies of the respective atomic (blue colour) and ionic (red colour) lines in eV. Data extracted from reference 21.

Table 2 Studies dealing with mixed gas Ar-N<sub>2</sub> plasmas in ICP OES

Element	Matrix	N <sub>2</sub> /Addition Mode	Remarks about the N <sub>2</sub> Effect	Reference
Cr, Co, Mo, Ni, Tl, Pb, Cd, Zn, V, As e Se	Aqueous solutions	0 - 100%/outer gas	Limits of detection (LODs) and signal/background ratio of ion and neutral atom lines of the high excitation energies, excited in a pure Ar-plasma, were superior to those observed in the Ar-N <sub>2</sub> plasma when pure N <sub>2</sub> was used in the outer gas flow; the opposite trend was observed for neutral atom lines of medium excitation energies.	13
Ag, Al, As, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mo, Ni, Se, e Zn	Aqueous solution	0 - 100%/outer gas	The N <sub>2</sub> -Ar-ICP volume was lower than that of Ar-ICP; the N <sub>2</sub> -Ar-ICP must be viewed more close to the induction coil; number of bands in the 300 to 500 nm interval of the emission spectra was reduced; N <sub>2</sub> addition worsened the ICP performance and LODs.	21
K, Mg, Ca, Pb, Cd, Zn	Aqueous solution	0 - 7%/outer gas	The analyte signal increased and the LODs were 5-10 times better; with the addition of 0.2 L min <sup>-1</sup> N <sub>2</sub> , the Mg (II)/Mg (I) ratio increased from 7 to 20.	22
-	-	0 - 100%/outer gas	Properties of N <sub>2</sub> -Ar-ICP were obtained by computer simulation; N <sub>2</sub> -Ar-ICP moves closer to the state of local thermodynamic equilibrium (LTE) as the concentrations of N <sub>2</sub> in the outer gas is increased; the LTE model predicts that the mixed-gas plasma has maximum temperatures (9900–10100 K) comparable with Ar-ICP (10600 K); the predicted temperature is reduced as the concentration of the molecular gas is increased; signals in N <sub>2</sub> -Ar-ICP must be monitored at observation height lower than that for Ar-ICP.	25
Mg, Ca, Ba, Zn, Cd, Fe e Y	Aqueous solution	0 - 0.6 L min <sup>-1</sup> /outer gas	The ternary composition Ar/He/N <sub>2</sub> improved the signal-to-noise ratio; He suppressed the background of nitrogen species; higher plasma power was required.	26
Ba, Mg, Cr, Co, Ni, Cd, Pb	0.5% (m/v) Na solution	5%/outer gas	The Mg (II)/Mg (I) ratio increased with the N <sub>2</sub> addition; suppression of the analytical signal was lower by using a direct injection high efficiency nebulizer (DIHEN) and N <sub>2</sub> addition.	27
-	Aqueous solution of Fe	0 - 100%/outer gas	Radially profiles of excitation temperature were computed using Fe as thermometric species; N <sub>2</sub> addition up to 10% increased the excitation temperature in 1000 K while total replacement of Ar by N <sub>2</sub> decreased the excitation temperature remarkably.	28
-	-	10%/outer gas	Addition of N <sub>2</sub> decreased by 30 % the electronic density in the central channel of the ICP; the size of the ICP was diminished.	29
Ca, Cd	Aqueous solution of Ca and Cd	0 - 100%/outer gas	The background signal increased due to NO formation; 10% (v/v) N <sub>2</sub> increased the signal-to-noise ratio for Cd.	30
Mg, Cd, Zn, Mn, Cu, Cr, Sr, Co	Aqueous test solution	0 - 100%/outer gas	Profiles of emission signals were collected at various distances above the induction coil; the use of 10% N <sub>2</sub> provided higher signal-to-noise ratio; total replacement of Ar by N <sub>2</sub> degraded the excitation capability of ICP.	31
Ca	Aqueous solution and phosphate matrix solution	0 - 100%/outer gas	The signal-to-noise ratio was better in plasma viewed close to the induction coil; N <sub>2</sub> addition mitigated phosphate matrix effects; interference of K on Ca was reduced; the linearity of calibration curve was preserved.	33
Cr, Co, Mo, Ni, Tl, Pb, Cd, Zn, V, As, Se	Aqueous solution	0 - 100%/nebulizer gas	The LODs were deteriorated	13
Ca	Aqueous solution	16.7%/ nebulizer gas	The central channel of the ICP was widened and shortened whereas the overall diameter of the ICP was not affected; drop of temperature (3000–5000 K) and gas-kinetic temperature were observed in the central channel; electron temperature increased in the toroidal zones of ICP when N <sub>2</sub> was concomitantly added to the intermediate flow. These combined effects caused a 20-fold depression in the calcium ion emission intensity.	17

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Table 2 (Continued)

Several emission lines (from 2 to 18 eV)	Aqueous solution	5%/nebulizer gas (ultrasonic nebulization)	Contribution of charge transfer from the foreign-gas ion was not important to the overall ionization and excitation of the analyte in the normal analytical zone of the plasma (NAZ) and at the concentration used; no evidence of charge transfer between the analytes and nitrogen species ( $N_2^+$ and $N^+$ ) was found; reaction of charge transfer between Ar and $N_2$ may occur.	20
V, Cu, Mn, Cr, Fe, Co, Ni, Cd, Pb, Zn, Mo, W, Pt, Pd, Zr, Au	Aqueous solution with 5% (m/v) Na, K or Ca	0 - 20 mL min <sup>-1</sup> / nebulizer gas	Plasma robustness (Mg(II)/Mg(I) increased from 14 to 20 for pneumatic nebulization, and 12 to 25 for pneumatic nebulization with aerosol desolvation; ionic lines were more affected than atomic lines; LODs for $N_2$ -Ar-ICP and Ar-ICP were almost similar; precision, accuracy and linearity of calibration curves were not degraded; addition of $N_2$ mitigated matrix effects.	23
-	Aqueous solution	0 - 40 ml min <sup>-1</sup> / nebulizer gas/after the spray chamber	The excitation temperature fell initially, but increased considerably for 10-40 ml min <sup>-1</sup> of $N_2$ ; the ratio (Mg (II)/Mg (I) increased from 7.5 to 12; the ICP extinguished when the $N_2$ flow was too high.	32
-	-	0-20%/nebulizer gas	Above 20% $N_2$ the high-temperature zone of the plasma shifted out; the predicted axial channel temperature raised steeply within the load coil, reached a peak near the top turn of the induction coil and then declined gradually at distances of 20-40 mm from the top of the injector tube; as the percentage of $N_2$ was increased, the axial channel widened; the hottest core of the mixed Ar- $N_2$ plasma shifted away from the axial channel; the maximum axial temperature was predicted to diminish when $N_2$ displaces Ar in the nebulizer gas flow; the plasma appeared to move away from the tip of the injector tube as $N_2$ was added; the presence of $N_2$ raised the observation height and increased the instability of the plasma whereas the axial temperature was reduced.	25
Ca	Aqueous solution	16.7%/intermediate gas	An increase of about a $1 \times 10^8$ electrons cm <sup>-3</sup> in the low toroidal regions of the plasma and gas-kinetic temperature about 1000 K throughout most of the discharge were observed; calcium ion emission intensity decreased 1.7-fold.	17

Table 3 Applications of mixed gas Ar-N<sub>2</sub> plasmas in ICP-MS

Analyte	Sample	N <sub>2</sub> /Addition Mode	Remarks of the N <sub>2</sub> Effect	Reference
Li, Ti, Co, Ba, Ce, Pb, U	Certified urine	1%/outer gas	Addition of 1% N <sub>2</sub> can eliminate <sup>40</sup> Ar <sup>35</sup> Cl <sup>+</sup> and dramatically reduce <sup>35</sup> Cl <sup>16</sup> O <sup>+</sup> and <sup>37</sup> Cl <sup>16</sup> O <sup>+</sup> , improving accuracy for V, As and Se and respective LODs.	35
Fe, Cu, Mo	Seawater (matrix separation/analyte preconcentration)	8%/outer gas	Production of <sup>40</sup> Ar <sup>16+</sup> in the ICP was reduced, allowing to measurement of <sup>56</sup> Fe <sup>+</sup> ; iron determination using isotope dilution was possible, with <sup>56</sup> Fe as the reference isotope and <sup>57</sup> Fe as the spike, using N <sub>2</sub> -Ar-ICP and partial aerosol desolvation.	37
As	Urine	1%/outer gas	Interference by <sup>40</sup> Ar <sup>35</sup> Cl <sup>+</sup> on <sup>75</sup> As <sup>+</sup> was reduced; accuracy and sensitivity were improved.	39
<sup>55</sup> Mn, <sup>56</sup> Fe, <sup>57</sup> Fe, <sup>60</sup> Ni, <sup>63</sup> Cu, <sup>66</sup> Zn, <sup>114</sup> Cd, and <sup>208</sup> Pb	Seawater (matrix separation/analyte preconcentration)	8%/outer gas	Production of <sup>40</sup> ArO <sup>16+</sup> in the ICP was reduced, allowing to measurement of low concentration of Fe by monitoring the <sup>56</sup> Fe <sup>+</sup> signal.	40
<sup>27</sup> Al, <sup>51</sup> V, <sup>52</sup> Cr, <sup>55</sup> Mn, <sup>56</sup> Fe, <sup>57</sup> Fe, <sup>59</sup> Co, <sup>60</sup> Ni, <sup>65</sup> Zn, <sup>65</sup> Cu, <sup>75</sup> As, <sup>76</sup> Se, <sup>78</sup> Se, <sup>98</sup> Mo, <sup>114</sup> Cd, <sup>121</sup> Sb, <sup>208</sup> Pb	0.1 or 0.01 mol L <sup>-1</sup> Na, river water	2 - 10%/outer gas	Analyte signal suppression was mitigated for a wide range of m/z, allowing the use of a single isotope as internal standard.	47
<sup>52</sup> Cr, <sup>55</sup> Mn, <sup>59</sup> Co, <sup>58</sup> Ni, <sup>65</sup> Cu, <sup>64</sup> Zn, <sup>75</sup> As, <sup>98</sup> Mo, and <sup>208</sup> Pb	Seawater 2-fold diluted (aliquots of 50 µL were introduced in the ICP)	4%/outer gas	Plasma operated at sampling depth 2 mm higher than that for optimal sensitivity provided robust operating conditions that greatly reduced matrix effects while still maintained sufficient sensitivity for analyte quantification; quantification of Mo was accurate; determination of other elements should be possible with more sensitive ICP-MS instruments.	49
As, <sup>51</sup> V, <sup>77</sup> Se, <sup>78</sup> Se <sup>+</sup>	Rice flour, citrus leaves, fish liver, seawater	2%/outer gas	The ArCl <sup>+</sup> interference on Se, As and V in presence of 1% Cl <sup>-</sup> was overcome with the addition of N <sub>2</sub> ; thermal pinch was observed.	54
Mo, U	Seawater	0.13%/outer gas + 0.09 L min <sup>-1</sup> as sheath gas around the nebulizer gas	Accurate determination of U and Mo in certified seawater using external calibration, without matrix-matching was possible (the spray chamber was maintained at 0°); oxide formation was completely suppressed; matrix effects were reduced; a two order of magnitude increase in background intensities was observed at m/z = 30 and 54, likely from <sup>14</sup> N <sup>16</sup> O <sup>+</sup> and <sup>40</sup> Ar <sup>14</sup> N <sup>+</sup> , respectively; background at m/z 55 and 56 increased presumably from <sup>40</sup> Ar <sup>14</sup> NH <sup>+</sup> (or <sup>40</sup> Ar <sup>15</sup> N <sup>+</sup> ) and <sup>40</sup> Ar <sup>15</sup> NH <sup>+</sup> , respectively; Ar <sub>2</sub> <sup>+</sup> formation was reduced.	18
Cu, Cd, Sb, <sup>56</sup> Fe, UO <sup>+</sup> /U <sup>+</sup>	Marine sediment, freshwater	8%/outer gas	Oxides were more efficiently reduced compared to partial aerosol desolvation or spray chamber cooling; interference by oxides and hydroxides was overcome; increased desolvation of the aerosol enhanced the beneficial effect of N <sub>2</sub> , allowing to determination of <sup>56</sup> Fe.	15
Li, Ti, Co, Ba, Ce, Pb, U	Certified urine	3%/nebulizer gas	Accuracy for V, As and Se was improved; interference by polyatomic ions was reduced; loss of sensitivity was observed in some extent.	35
As	Urine, tomato leaves, fish tissue	32 mLmin <sup>-1</sup> /nebulizer gas	Interferences by Ar and Cl polyatomic were reduced; accuracy and sensitivity were improved.	36
<sup>202</sup> Hg: <sup>199</sup> Hg ratio	Soil	0.5%/nebulizer gas	The sensitivity was 4 - 6-fold increased by addition of N <sub>2</sub> .	38
As	Urine	3%/nebulizer gas	Interference by <sup>40</sup> Ar <sup>35</sup> Cl <sup>+</sup> on <sup>75</sup> As <sup>+</sup> was reduced; accuracy and sensitivity were improved.	39
As, <sup>51</sup> V, <sup>77</sup> Se, <sup>78</sup> Se <sup>+</sup>	Rice flour, citrus leaves, fish liver, seawater	0-8%/nebulizer gas	The ArCl <sup>+</sup> interference on Se, As and V in presence of 1% Cl <sup>-</sup> was removed; better results were obtained for 4.5% N <sub>2</sub> in the nebulizer gas where interferences by MO <sup>+</sup> and ArO <sup>+</sup> were reduced; plasma shrank away from both sampler cone and torch when N <sub>2</sub> was added; the central channel of ICP became wider	54

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Table 3 (Continued)

As	Rice wheat, citrus leaves, fish liver	4 -5%/nebulizer gas	Production of ArCl was reduced; accurate determination of As was possible even in presence of 1000 mg L <sup>-1</sup> Cl <sup>-</sup> .	42
<sup>58</sup> Ni, <sup>55</sup> Mn, <sup>59</sup> Co, <sup>63</sup> Cu, <sup>64</sup> Zn, <sup>208</sup> Pb	Seawater	0.8%/nebulizer gas	The interference of <sup>40</sup> ArNa <sup>+</sup> on m/z 63 was overcome; sensitivity was reduced; signal-to-noise ratio and LODs were improved.	45
Several isotopes (m/z 11 - 238)	Peach leaves, lobster hepatopancreas, mussel tissue, oyster tissue, mixed diet, 0.05% (m/v) HCl	8%/nebulizer gas	The LODs were, on average, 2-3 times higher for N <sub>2</sub> -Ar-ICP; N <sub>2</sub> addition decreased interference by polyatomic ions (mainly from ArCl <sup>+</sup> , ClO <sup>+</sup> and Cl <sub>2</sub> O <sup>2+</sup> ) and improved the accuracy of the results; the oxide levels were reduced to 0.6%.	51
Pt	Environmental, food and biological samples	0 - 1.5%/nebulizer gas	The level of HfO that interferes on Pt was reduced; sensitivity and signal stability were improved. The beneficial effects were observed in the range from 5 to 15 mL min <sup>-1</sup> N <sub>2</sub> ; a nebulizer/aerosol desolvation system was used for introducing the solution in the ICP.	57
As	Drinking water	0.5 - 5%/nebulizer gas	Nitrogen additions of more than 2% reduced the As signal without further improving the As/ArCl ratio; addition of 2% N <sub>2</sub> yielded the best results and reduced the ArCl signal by a factor of about 5; hydride generation associated with ICP-MS was used.	58
Rare earth elements (REEs)	Natural water (preconcentration using iron hydroxide)	120 ml min <sup>-1</sup> /intermediate gas	Interference by polyatomic oxide ions was reduced and the sensitivity increased.	48
As, <sup>51</sup> V, <sup>77</sup> Se, <sup>78</sup> Se <sup>+</sup>	Rice flour, citrus leaves, fish liver, seawater	2%/intermediate gas	Reduction of interference was minimal; tolerance for N <sub>2</sub> was limited to 3%; plasma shrank away from both sampler cone and torch when N <sub>2</sub> was added; the central channel of ICP became wider.	54

Table 4 Studies and applications of mixed gas Ar-N<sub>2</sub> plasmas in LA-ICP-MS

Analyte	Sample	N <sub>2</sub> /Addition Mode	Remarks of the N <sub>2</sub> Effect	Reference
<sup>53</sup> Cr, <sup>55</sup> Mn, <sup>59</sup> Co, <sup>66</sup> Zn, <sup>71</sup> Ga, <sup>88</sup> Sr, <sup>90</sup> Zr, <sup>93</sup> Nb, <sup>181</sup> Ta, <sup>232</sup> Th, <sup>238</sup> U, REEs	Geological reference materials (fused)	2.9%/carrier gas in the ablation cell	Sensitivity increased about 2.4 fold.	68
<sup>140</sup> Ce <sup>+</sup> , <sup>232</sup> Th <sup>+</sup> , <sup>156</sup> CeO <sup>+</sup> , <sup>248</sup> ThO <sup>+</sup>	Gel standard (mixed with carbonaceous binder and pressed)	About 1%/principal gas, 12%/carrier gas in the ablation cell	Addition N <sub>2</sub> to the principal gas increased the sensitivity and reduced MO <sup>+</sup> /M <sup>+</sup> ratio; addition of about 12% N <sub>2</sub> to the ablation cell had a similar effect, being greatest at a higher forward rf plasma power (1700 W); on addition of N <sub>2</sub> to the plasma gas the diameter of the central channel was visibly reduced.	69
<sup>111</sup> Cd, <sup>114</sup> Cd, ThO <sup>+</sup> /Th <sup>+</sup> (as diagnostic tool)	Glass	5-10 mL min <sup>-1</sup> /carrier gas in the ablation cell	The sensitivity for Cd increased by a factor of 3 and oxide interferences decreased by one order of magnitude; the significant increase of NO <sup>+</sup> signal suggested that removal of oxygen through NO formation was the main reason for the reduction of ThO <sup>+</sup> .	70
<sup>176</sup> Hf/ <sup>177</sup> Hf	Zircon	2-4 ml min <sup>-1</sup> /carrier gas in the ablation cell	Precision and accuracy for Hf isotopic ratio determination using MC-ICP-MS (multichannel-inductively coupled plasma-mass spectrometry) were improved; sensitivity was improved and non-linear instrumental mass fractionation for Hf was reduced; <sup>176</sup> Yb/ <sup>177</sup> Hf and <sup>176</sup> Lu/ <sup>177</sup> Hf ratios decreased, which would aid accurate determination of Hf isotopes in high-content Yb and Lu samples.	71
<sup>176</sup> Hf/ <sup>177</sup> Hf, Lu e Yb	Zircon	4 ml min <sup>-1</sup> /carrier gas after the ablation cell	Precision of Hf isotope microanalysis for zircon samples by MC-ICP-MS was improved; sensitivity for Hf, Lu and Yb increased by a factor of 2-3; measured <sup>173</sup> Yb/ <sup>177</sup> Hf ratio changed with the addition of N <sub>2</sub> , suggesting the different behaviour P between Yb and Hf in ICP; the Lu/Hf ratio did not vary measurably even with the addition of N <sub>2</sub> , indicating that N <sub>2</sub> addition did not cause elemental fractionation between Hf and Lu.	72
<sup>205</sup> Tl/ <sup>203</sup> Tl, <sup>206</sup> Pb/ <sup>204</sup> Pb, <sup>207</sup> Pb/ <sup>204</sup> Pb, <sup>208</sup> Pb/ <sup>204</sup> Pb, <sup>208</sup> Pb/ <sup>206</sup> Pb, <sup>207</sup> Pb/ <sup>206</sup> Pb	Certified glass	0-20 ml min <sup>-1</sup> /carrier gas before the ablation cell	The signal intensity of Tl increased by a factor of 4 and Pb by a factor of 3 at N <sub>2</sub> flow rate of 5 ml min <sup>-1</sup> using femtosecond (fs) laser associated with MC-ICP-MS; abundance of doubly charged ions increased; mass bias was 13% reduced for Tl and Pb at constant N <sub>2</sub> flow rate of 8 ml min <sup>-1</sup> ; oxides level was reduced; background for lighter isotopes ( <sup>29</sup> Si, <sup>31</sup> P, <sup>39</sup> K, <sup>55</sup> Mn and <sup>66</sup> Zn) were found to increase; polyatomic species of nitrogen increased.	73
<sup>139</sup> La, <sup>140</sup> Ce, <sup>141</sup> Pr, <sup>146</sup> Nd, <sup>147</sup> Sm, <sup>151</sup> Eu, <sup>157</sup> Gd, <sup>159</sup> Tb, <sup>163</sup> Dy, <sup>165</sup> Ho, <sup>166</sup> Er, <sup>169</sup> Tm, <sup>172</sup> Yb, <sup>175</sup> Lu)	Synthetic CaCO <sub>3</sub> standards, doped with analytes, carbonatite, glass standards	5 ml min <sup>-1</sup> /carrier gas, after the ablation cell	The sensitivity of <sup>140</sup> Ce <sup>+</sup> increased by 30% (the N <sub>2</sub> flow was optimized by maximizing the <sup>140</sup> Ce signal); ablation in He atmosphere and addition of N <sub>2</sub> to the carrier gas effectively reduced matrix effect (between carbonate and silicate glasses).	74
Y, Cs, Ce, Tb, Tm, Ta, and e respective oxides	Silicate disks (silicon dioxide fusion by adding REEs oxide powders), metal	0 - 20 ml min <sup>-1</sup> /carrier gas, after the ablation cell	Little to no sensitivity enhancement with the addition of N <sub>2</sub> was found (a sector field instrument and an ICP torch with a grounded shield were used); the NAZ became tinner, diminishing the radial diffusion of ions and yielding optimum M <sup>+</sup> signals; lowest MO <sup>+</sup> /M <sup>+</sup> signal ratio and highest T <sub>gas</sub> values at the position sampled in the ICP were found; the MO <sup>+</sup> /M <sup>+</sup> signal ratio decreased by maximizing atomic sensitivity at lower total gas loads; the abundance of MO <sup>+</sup> ions during LA was reduced.	75
Pb isotope ratio ( <sup>208</sup> Pb/ <sup>206</sup> Pb, <sup>206</sup> Pb/ <sup>207</sup> Pb)	Glass, silicate and sulfide minerals	38 ml min <sup>-1</sup> /carrier gas, prior to the sample cell	The sensitivity was increased and mass bias reduced; precision and accuracy of isotope ratio were improved.	76
Be, B, Ge, As, Mo, Rh, Pd, Ag, Cd, In, Sn, Sb, W, Re, Ir, Pt, Au, Tl, Bi	Certified glass	5 ml min <sup>-1</sup> /carrier gas, downstream from the cell	Wider axial ions distribution was observed; signal enhancement was highly dependent on the sampling depth; sensitivity was, in general, 1.4 - 3 fold increased; LODs were improved (by factors of 1.2 - 2.5) and oxide level (ThO <sup>+</sup> /Th <sup>+</sup> ) reduced to 0.02% at sampling depth of 6 mm; ICP-induced fractionation could be minimized (U <sup>+</sup> /Th <sup>+</sup> ≈ 1) with no loss of sensitivity.	77

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Table 4 (Continued)

47 elements	Certified glass	0 - 10 ml min <sup>-1</sup> / carrier gas, upstream from the sample cell	Addition of N <sub>2</sub> did not enhance the sensitivity of most elements; a weak sensitivity increase was only found for a few heavy elements such as Au, U and Pb, while other elements were unaffected or lost sensitivity with increasing N <sub>2</sub> flow; the change of the plasma geometry and sampling position were not investigated in detail.	78
65 elements	Certified glass	5 - 10 ml min <sup>-1</sup> / carrier gas, downstream from the sample cell	The sensitivity for most investigated elements increased 2 to 3 times - the degree of enhancement depended, to some extent, on the 1 <sup>st</sup> ionization energy; oxides and hydrides were reduced by an order of magnitude and 3 times, respectively; Ca <sup>2+</sup> signal increased; the background signal at m/z 29, 31, 42, 51, 52 and 55 increased due to polyatomic nitrogen ions increase; addition of 5 ml min <sup>-1</sup> N <sub>2</sub> led to significant wider axial profiles and more uniform distribution of ions with different physical and chemical properties; a very consistent increase of Ar signal by the addition of N <sub>2</sub> indicated better energy transfer effect by N <sub>2</sub> in the plasma.	79
Abundances of <sup>206</sup> Pb, <sup>207</sup> Pb, <sup>204</sup> Pb, <sup>238</sup> U (for U- Pb isotope geochronology)	Zircon	0.41 ml min <sup>-1</sup> / carrier gas	N <sub>2</sub> addition was carried out just for enhancing the sensitivity.	80
REEs, Hf, U, PGEs, Re	Zircon	0.4 ml min <sup>-1</sup> /carrier gas, in the sample cell	The addition of N <sub>2</sub> increased the sensitivity for high-mass isotopes	81