White Paper

Economical Carbon Enhanced Plasma Ionization: Substituting Acetic Acid with Carbon Dioxide

Cost-effective method suitable for routine analysis of Australian grain export cargoes by Agilent 8900 ICP-QQQ

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Introduction

Commercial laboratories must deliver competitively priced sample analysis to maintain client work, so reducing the cost per analysis can help secure repeat business. In our lab, we routinely add carbon to the plasma of our ICP-MS to optimize the performance of the instrument for the analysis of grain samples. To reduce reagent costs per sample, we investigated modifying the plasma of our Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) using low-cost carbon dioxide (CO_2) rather than acetic acid.

It is well known that a carbon-enhanced plasma increases the signal of some elements, notably arsenic (As), selenium (Se), and phosphorus (P), although the precise mechanism of the enhancement is not clearly understood.[1] Doping the plasma with a source of carbon facilitates a more complete ionization of analytes with lower ionization energies than carbon.[2] This carbon enhancement process facilitates a more comprehensive analysis, contributing to the sensitivity and accuracy of our multi-element method.

Carbon can be added to the plasma using a liquid source that is miscible with water, such as methanol, ammonium carbonate, isopropanol, acetic acid, and other similar compounds. Typically, one of these chemicals is added with the sample diluent or via the internal standard (ISTD) line and mixed with the sample using a tee-piece. Using a final carbon content in the sample aerosol of approximately 1% and depending on the carbon source used, the enhancement factor for As can be as high as a fourfold increase in signal-to-noise.[2]

Given the sensitivity of ICP-MS, adding carbon to the plasma requires a sufficiently pure source to avoid sample contamination and to prevent introducing interferants into the background noise. For routine analysis of food samples, for example, the cost of acquiring a high-purity liquid source of carbon to modify the plasma is prohibitively expensive. In contrast, delivering the equivalent amount of carbon using CO_2 gas is cost-effective, once the initial costs of the gas delivery system have been accounted for.

To ensure that the carbon content can be introduced into the total argon flow of the plasma reproducibly, the CO_2 must first be blended with argon (Ar). An existing fifth plasma gas control line and mass flow controller (MFC) of the 8900 ICP-QQQ was used to introduce the gas at a flow rate of between 0 to 1 L/min into the torch connector. The connector is positioned just before the torch, allowing the gas to mix with the sample aerosol before analysis.

Dynamic gas blending is common in the beverage delivery industry, so a commercially available system was used in this study to supply 10% CO_2 in Ar to the plasma of the ICP-QQQ. However, a significantly higher flow rate is required for accurate dilution of the CO_2 into Ar than the 1 L/min maximum setting of the option gas flow controller of the instrument. To achieve the required 160 L/min gas flow, a ballast tank was used for high-flow filling and storage.

In this study, we analyzed digests of grain samples using the 8900 ICP-QQQ with a carbon-modified plasma, aiming to optimize the instrument's performance while minimizing laboratory reagent costs. Comparison data is provided for the effectiveness of using CO_2 versus acetic acid as the carbon source for plasma modification. By investigating these two methods, we demonstrated the advantages of CO_2 in terms of cost-effectiveness while maintaining analytical performance for the practical implications of commercial laboratories, where cost efficiency is crucial for securing repeat business.

Experimental

System configuration

A gas mixer system supplied by Beverage Systems Ltd (BSL, Kent, UK) was used to blend CO_2 and Ar (Figure 1).

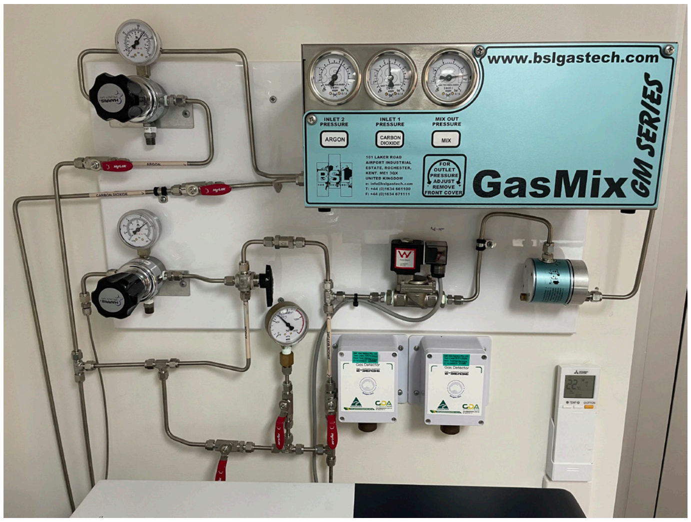

Figure 1. Installation of the gas mixing system (BSL) used to blend carbon dioxide and argon.

As shown in Figure 2, a high purity (4.5 N) G sized bottle of CO_2 was connected to a regulator to feed the gas mixer at 100 bar. 5.0 N Ar regulated at 90 bar was supplied to the gas mixer from the existing argon pressurized liquid vessel (PLV) supply that feeds the argon gas to the ICP-QQQ in our lab. Once mixed, the gas leaves the mixer and enters an MFC. The MFC ensures that the flow rate remains constant, so that the ratio of the gas can be precisely controlled to the target percentage of CO_2 in Ar. From the MFC, the gas fills a ballast tank, which is fitted with a pressure sensor that automatically triggers a refill when the gas level is low. This automated process ensures that the mixer can fill the ballast tank using a relatively high optimal mixer flow rate and store enough gas for several days of analyses.

The ICP-QQQ draws gas from the ballast tank (a repurposed 265 L PLV) via the option gas feed to the plasma using a flow rate between 0 to 0.1 L/min at a pressure of 60 kPa. This ballast tank size allows for more than 48 hours of continuous running and therefore provides stable in-batch CO_2 levels.

The following points were important to the success of the process:

- Venting: the ballast tank was fitted with a vent to purge the ballast to waste to avoid contamination during setup and maintenance.
- Bypassing the mixer and ballast tank: a three-way valve was installed before the ICP-QQQ that enabled Ar to be supplied directly to the ICP-QQQ, without CO_2 present in the option gas. This facility ensures that any troubleshooting could be conducted using the original instrument tune conditions.

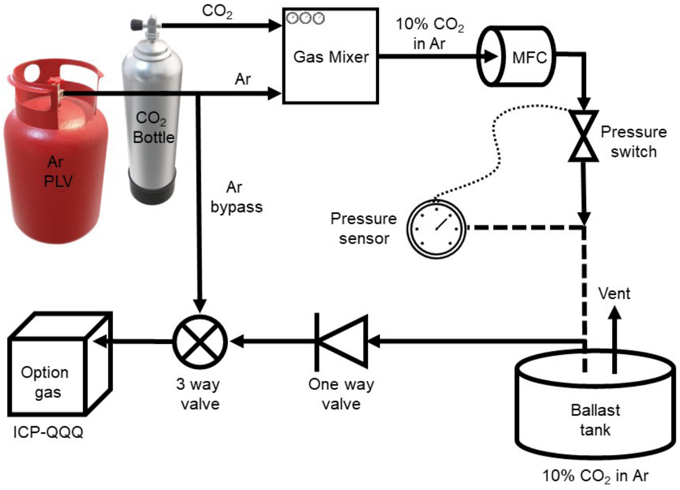

Figure 2. Schematic diagram of the process for mixing carbon dioxide in argon, storing the gas in a ballast tank, and delivering the gas to the plasma of the Agilent 8900 ICP-QQQ via a three-way valve.

Economic analysis

To evaluate the economic case for using CO_2 compared to acetic acid, the ongoing costs of both reagents were calculated, along with upfront expenses of buying and installing the gas mixing equipment. As shown in Figure 3, the payback period for the CO_2 system is around six years, based on current Australian dollar (AUD) prices. The figure also highlights significant long-term savings of the CO_2 system over 20 years, which is the approximate lifetime of the CO_2 bottle.

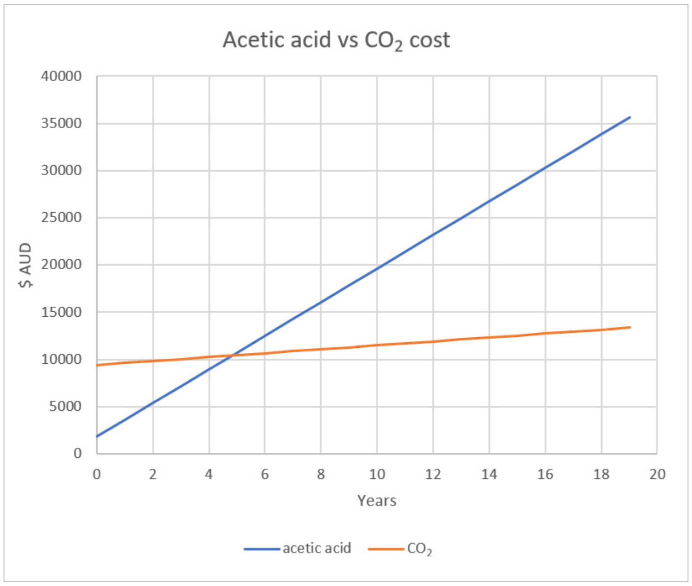

Figure 3. Cost of using acetic acid for carbon enhancement versus the cost of using a 10% ballast mix of CO_2 over 20 years, inclusive of initial CO_2 installation costs. All costs were in Australian dollars.

Instrumentation

An Agilent 8900 Advanced configuration ICP-QQQ, which includes a fifth plasma gas control line for the addition of alternative gases or mixed gases, was used. This fifth option gas mass flow controller (Agilent part number G5720A) is available as an accessory for Agilent ICP-MS instruments including the Agilent 8900 Standard configuration, 7900 ICP-MS, or 7850 ICP-MS.

To ensure tolerance to any suspended particulates remaining in the extracts of grain-samples, the 8900 ICP-QQQ was fitted with a PEEK Mira Mist parallel path nebulizer. The remainder of the sample introduction system was standard, comprising a Peltier cooled, Scott type, double-pass, quartz spray chamber and torch (2.5 mm id injector). Pt-tipped interface cones were used in place of the standard Ni cones.

The 8900 ICP-QQQ includes an Ultra High Matrix Introduction (UHMI) aerosol dilution system and two scanning quadrupoles (Q1 and Q2) positioned either side of the Octopole Reaction System (ORS^4) collision/reaction cell (CRC). The 8900 was operated in both single quadrupole (SQ) mode and triple quadrupole (ICP-QQQ or MS/MS) mode. In SQ mode, the CRC was pressurized with helium (He) cell gas to attenuate the transmission of many common polyatomic ions. As this setup is the standard operation mode of Agilent single quadrupole ICP-MS instruments, the method could be applied to the 7850 or 7900 ICP-MS for elements reported in SQ mode. In MS/MS mode, the CRC was pressurized with hydrogen (H_2) and nitrous oxide (N_2O) cell gases to provide mass-shift and on-mass analysis of selected analytes. The 8900 ICP-QQQ effectively uses reactive cell gases and ion/molecule reaction chemistry with MS/MS mode to resolve difficult spectral interferences.[2] The superior interference removal offered by reaction chemistry with MS/MS is beneficial for the analysis of elements such as As that are subject to problematic interferences in routine applications, including the analysis of cereals and oilseeds.

The main 8900 ICP-QQQ operating conditions are shown in Table 1.

Table 1. Agilent 8900 ICP-QQQ operating conditions.

Parameter	Value	
ICP-QQQ Mode	Single Quad	MS/MS
Plasma RF Power (W)	1550	
Sampling Depth (mm)	9	
Carrier Gas Flow Rate (L/min)	0.80	
Option Gas Flow Rate (%)	15	
Spray Chamber Temp (°C)	2	
He Cell Gas Flow Rate (mL/min)	5.0	0.0
H_2 Cell Gas Flow Rate (mL/min)	–	3.0
N_2O Cell Gas Flow Rate (%)	–	11
Kinetic Energy Discrimination (KED) (V)	5.0	–7.0
Axial Acceleration (V)	–	1.5

Aerosol generation and nebulization efficiency

An initial comparison experiment was conducted between the acetic acid and CO_2 methods at a calculated equivalent final carbon content in the plasma of 1%. The results (counts per second) for an As standard at various concentrations using the plasma enhanced methods and an Ar-only plasma are shown in Table 2. N_2O was used in the CRC to react with As, enabling measurement of AsO at mass 91 by ICP-QQQ. The mass-shift method avoided polyatomic ion interferences such as $^{40}Ar^{35}Cl^+$, $^{36}Ar^{38}ArH^+$, and $^{36}Ar^{39}K$ at mass 75. These interferences can also be reduced using a single quadrupole ICP-MS method operating in helium collision mode via a kinetic energy discrimination (KED) mechanism.[3]

Table 2. Comparison of measured counts for arsenic at different concentrations using the Agilent 8900 ICP-QQQ with a carbon enhanced plasma achieved by adding carbon dioxide (10% CO_2 in Ar) and 20% acetic acid, and with an Ar-only plasma.

	Source of Carbon		No Carbon
Concentration of As 75 -> 91 [N_2O] (µg/L)	Ballast Tank, 10% CO_2 in Ar (counts)	20% Acetic Acid (counts)	Bypass [Ar only] (counts)
0	301	251	159
0.05	521	428	226
0.5	2587	2065	658
5	24860	13765	5396

The vapor pressure and density properties of CO_2 and acetic acid affect the performance of the plasma. Acetic acid exhibits a higher vapor pressure of 0.0201 atm and a density of 1.05 g/cm^3 than water, which possesses a vapor pressure of 0.01 atm and a density of 1.00 g/cm^3 (Figures 4 and 5). So, nebulization of the 20% acetic acid solution, introduced to the plasma as an ISTD solution, yields greater aerosol generation for a given nebulizer gas flow, as shown in Figure 5. Conversely, aspirating an ISTD devoid of the 20% acetic acid leads to a diminished liquid vapor pressure, altering the nebulization dynamics of the sample. This change manifests as a reduction in matrix loading on the plasma, denoted by a decrease in the CeO/Ce ratio, see Figure 6. Such optimization enables adjustment of the nebulizer flow rate to 0.80 L/min, supplemented by the addition of 10% CO_2 at a rate of 15% of 1 L/min for the optional gas flow, thereby ensuring an equivalent total gas flow to the torch of 1.05 mL/min, as shown in Figure 6.

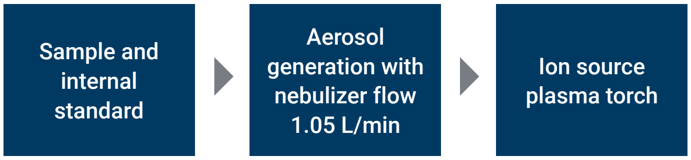

Figure 4. Flow diagram of the routine sample introduction process. No carbon enhancement, shown in blue, low matrix loading on the plasma.

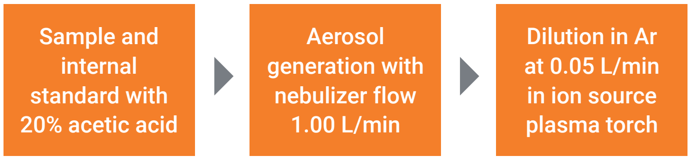

Figure 5. A flow diagram demonstrating the advantage of carbon enhancement achieved by adding the carbon source (acetic acid) with the internal standard. Carbon now flows throughout the process (shown in orange). As a result of the higher vapor pressure of acetic acid, the nebulization improves, yielding a greater aerosol generation for a given nebulizer gas flow. Acetic acid provides the carbon enhancement we are looking for, with the drawback of a higher matrix loading on the plasma, so a small amount of dilution gas is added to reduce matrix effects.

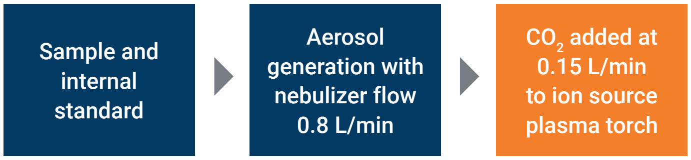

Figure 6. A flow diagram demonstrating the advantage of the carbon enhancement with CO_2 achieved by adding the carbon source as an option gas in the ion source, as shown in orange. This approach optimizes routine matrix loading but with all the performance of carbon enhancement in the plasma.

Dead volume of CO_2 delivery and stabilization time

Another advantage of using CO_2 rather than acetic acid is that the carbon can quickly and easily be removed from the system. The delivery system dead volume was measured by monitoring the As carbon-enhancement reaction. The time was recorded between the signals measured in an Ar-only plasma at a 0.1 mL/min flowrate into the ICP-QQQ and the carbon enhanced plasma. The gases were controlled using the three-way switch shown in Figure 2.

As shown in Figure 7, a dead volume time of 22 s was noted. This was the time between switching the three-way valve from the Ar-bypass position to adding 10% CO_2 in Ar from the ballast tank and the increase in As counts at a flow rate of 15% optional gas. Knowing that the total switching time (marked by the dotted lines in Figure 7) was 80 s, allows the stabilization time to be calculated (the time from when the valve was switched to the time the plasma was stable). This stabilization time was 58 s: 80 s minus the 22 s of dead time for the CO_2 to reach the plasma (as the gas traverses the regulator, 1/8-inch tubing, and option gas plumbing). A short stabilization time allows for the rapid removal of carbon and therefore carbon-based interferences, something that is not as readily done with a liquid carbon source. Additional carbon can be problematic, especially for samples with a high carbon content such as organic matrices, where interference from carbon-based compounds may affect accuracy and precision of measurements, particularly when using a single quadrupole ICP-MS or when some samples may not benefit significantly from carbon-enhanced techniques.

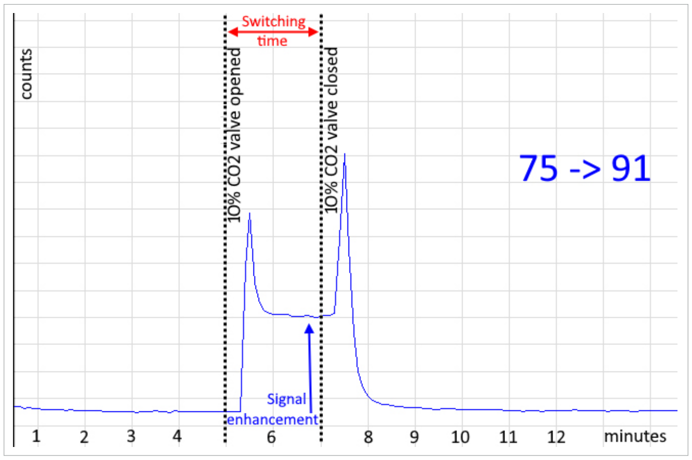

Figure 7. Monitoring of As 75 -> 91 signal during the switch from an Ar-only plasma to a CO_2 enhanced plasma and back to an Ar-only plasma. Switching was controlled using the three-way valve.

Results and discussion

Evaluation of signal enhancement

To evaluate the signal enhancement of adding CO_2 to the plasma for a variety of elements, 1 mL of each of the two Agilent PA tuning solutions (p/n 5188-6524) were diluted to 50 mL in 3% NHO_3 to give the element concentrations as listed in Table 3.

Table 3. Element concentrations for evaluation of carbon enhancement.

Element	Final Dilution Concentration (mg/L)
As, Be, Cd, Zn	0.04
Ge, Mo, Pd, Ru, Sb, Sn, Mg, Ni, Pb	0.02
Ir, Ti, Al, Ba, Bi, Co, Cr, Cu, In, Li, Lu, Mn, Na, Sc, Sr, Th, Tl, U, V	0.01
Y, Yb	0.005

The enhancement factors for selected elements using different concentrations of CO_2 in Ar (5.4, 8.1, 8.4, and 13.4%) delivered to the plasma from the ballast tank are given in Table 4. Figure 8 illustrates a significant enhancement of the signal for As in the presence of CO_2, supplied from the ballast tank, with optimal levels between 5 and 9%, peaking at approximately 8%. The introduction of the ballast gas into the plasma at a flow rate of 15% optional gas equates to a final carbon content within the plasma of 0.75 to 1.35%, with a peak of 1.2%.

Table 4. A selection of the most prominent elemental enhancement factors for carbon at various ballast tank percentages, when measuring the PA tuning solutions diluted to 50 mL in 3% NHO_3 (n=7).

Element	Cell Gas	5.4% CO_2	8.1% CO_2	8.4% CO_2	13.4% CO_2
7 Li	He	1	2.5	1.1	0.6
9 Be	He	1.7	3	1.8	1.1
10 B	No gas	0.9	2.3	1	1
11 B	No gas	3.4	3	3.7	1.9
24 Mg*	He	3.1	1.9	2.8	2.1
32 -> 48 S	N_2O	1.6	2.3	2.2	1.3
48 -> 64 Ti	N_2O	1.2	1.9	1	0.6
51 -> 51 V	N_2O	0.6	3.9	0.7	0.4
52 Cr*	He	1.2	1.9	1.2	0.8
59 -> 59 Co	N_2O	1.2	2.2	1.4	0.8
60 Ni	He	1.2	2.2	1.3	0.7
63 Cu	He	1.3	2.1	1.3	0.8
66 Zn	He	2.1	2.5	2.1	1.3
72 -> 89 Ge (ISTD)	N_2O	1.3	2.4	1.5	0.8
75 -> 91 As	N_2O	5.2	6.3	5.7	3.2
88 -> 88 Sr	N_2O	1.1	2.2	1.3	0.8
98 -> 98 Mo	N_2O	1.3	2.2	1.2	0.7
101 Ru	He	1.3	2.1	1.2	0.7
101 -> 101 Ru	N_2O	1.2	2.1	1.2	0.7
105 Pd	He	1.5	1.9	1.3	0.8
105 -> 105 Pd	N_2O	1.6	1.7	1.4	0.8
111 -> 111 Cd	N_2O	1.9	2.8	2.2	1.3
115 -> 115 In (ISTD)	N_2O	1.3	2.3	1.5	0.9
121 Sb	He	1.6	1.9	1.4	0.9
172 -> 172 Yb	N_2O	1.3	2.6	1.6	0.9
175 -> 175 Lu	N_2O	1.2	2.1	1.4	0.9
193 Ir (ISTD)	He	1.3	2.1	1.2	0.8
205 Tl	He	1.2	1.9	1.2	0.9
209 Bi (ISTD)	He	1.4	1.9	1.3	0.9

* Carbon-based interference.

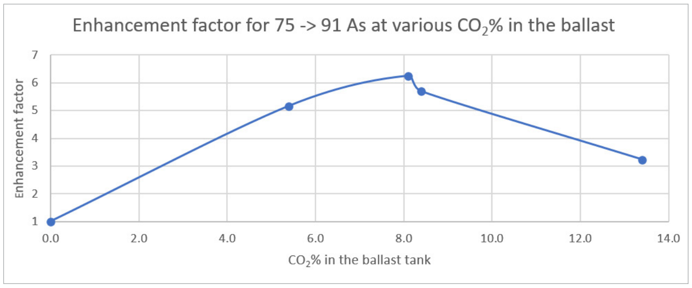

Figure 8. Enhancement factor for 75 -> 91 As at various percentage levels of CO_2 in Ar in the ballast tank (n=7).

Effects of easily ionized elements

The PA tuning solutions were used to study the effects of varying sodium levels via the addition of sodium nitrate. A series of solutions was prepared using different diluents comprising: 3% NHO_3, 0.5% Na and 3% NHO_3, 1% Na and 3% NHO_3, and finally 2% Na and 3% NHO_3. Each dilution was made at a ratio of one part in ten.

The ionization potential of carbon (11.26 eV) is higher than that of sodium (5.14 eV), which is an easily ionized element (EIE). The carbon in the plasma helped to maintain the sensitivity of elements such as Pb, As, and Cd by buffering against the disturbed electron equilibria caused by the EIE. A supply of 5.4% CO_2 in Ar in the optional gas feed to the ICP-QQQ provided the most benefit, as shown in Table 5.

Phosphorus (P) has also been included in Table 5 for reference to the additional dynamics occurring in the plasma that need to be considered. There is an enhancement that occurs because Na ions can increase the ionization efficiency of P in the plasma, leading to a higher signal intensity. The addition of 5.4% CO_2 in Ar in the optional gas attenuates the Na enhancement of the P at a 2% sodium concentration in the sample. This is an excellent example of why rapid removal of the carbon in the plasma is beneficial for analysis of some elements in high Na matrices (such as seawater samples) and demonstrates the advantage of using CO_2 supplied carbon over liquid supplied options, like acetic acid, to expand the flexibility of the total system.

Table 5. Signal suppression for Pb, As, Cd, and enhancement of P at various sodium concentrations normalized to the signal obtained with no added sodium (n=7).

Element	No Added Na	0.5% Na	1% Na	2% Na
31 -> 47 P	100	249	366	711
+ 5.4 % CO_2	100	247	350	430
+ 8.4 % CO_2	100	261	350	607
75 -> 91 As	100	96	73	59
+ 5.4 % CO_2	100	102	107	87
+ 8.4 % CO_2	100	74	58	49
111 -> 111 Cd	100	80	57	44
+ 5.4 % CO_2	100	100	104	85
+ 8.4 % CO_2	100	78	62	54
208 Pb	100	93	78	62
+ 5.4 % CO_2	100	101	104	86
+ 8.4 % CO_2	100	77	60	51

Carbon-based interferences

To check the effects of carbon on the analysis of magnesium (^{24}Mg) and chromium (^{52}Cr), both elements were monitored by analyzing the PA tuning solution with increasing % of CO_2 in Ar added to the plasma. The background levels for both elements can be affected by C_2 (*m/z* 24) and ArC (*m/z* 52), respectively. Figure 6 shows that the concentration of CO_2 in the ballast tank should be below 10% to minimize the background levels of C_2 and ArC, ensuring the accuracy and reliability of the Mg and Cr results.

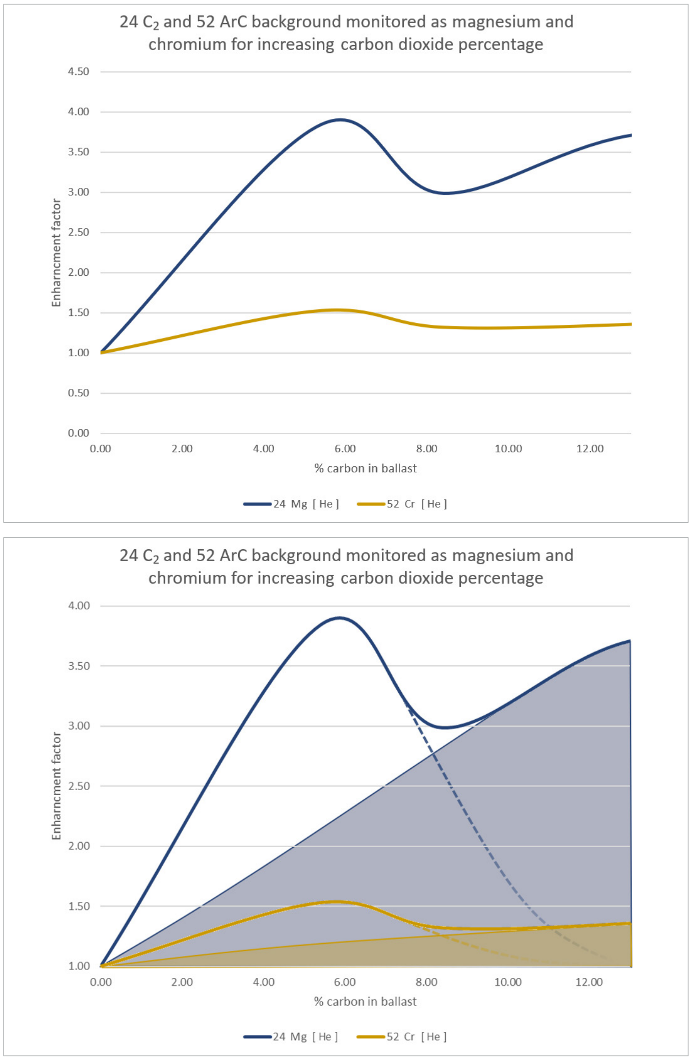

Figure 9. Monitoring of background levels at *m/z* 24 for C_2 interference on ^{24}Mg and *m/z* 52 for ArC interference on ^{52}Cr (n=7). Signal enhancements are plotted as solid line for mass 24 and 52. The shaded background shows competing contribution from carbon-based interferences that swamp the carbon enhancement of Mg and Cr as the CO_2 concentration in the plasma increases and the dotted line demonstrates probable continuation for the enhancement factor of Mg and Cr.

Optimal ballast tank concentration of carbon dioxide

The optimal ballast tank concentration of CO_2 in Ar for a multi-element analysis, taking EIEs into account, has been demonstrated to be around 5%, which provides around 0.75% carbon within the plasma. Adding 5% CO_2 to the plasma yields an advantageous enhancement of the ionization of numerous elements, including As with a 5.2x enhancement, as shown in Table 4. While greater enhancement factors can be achieved at even higher percentages of CO_2, the introduction of oxygen molecules from the CO_2 into the plasma starts to have a more pronounced negative impact. This is evident when compared to acetic acid, where the total oxygen availability is restricted to the central plasma. Presumably, CO_2 disperses oxygen molecules more thoroughly throughout the plasma, facilitating the formation of metal oxide ions ($M^{16}O^+$) which appear as interferences in the spectrum at *m/z* +16. Future investigations may focus on confirming this hypothesis by monitoring transitions such as P 31 -> 31 and PO 47 -> 47.

Our recommendation is to maintain a carbon content of around 5% CO_2 in Ar in the ballast tank to maximize benefits from carbon enhancement for multi-element analysis, while minimizing the adverse effects of additional oxide formation in the plasma. Also, the presence of CO_2 offers a protective effect against additional matrix loads, as evidenced by the addition of sodium nitrate, as shown in Table 5. For instance, for ^{208}Pb, 5.4% CO_2 in Ar results in relatively consistent responses across varying sodium concentrations compared to no added CO_2 or higher (8%) CO_2 in Ar content in the ballast tank.

Conclusion

A custom process was developed for mixing carbon dioxide in argon and supplying it to the plasma of the Agilent 8900 ICP-QQQ. The study showed that the use of gaseous carbon for plasma ionization enhancement provided advantages over traditional liquid sources of carbon, such as acetic acid, in terms of cost and performance. The scalability of the gas supply system can be enhanced by increasing the size of the ballast tank, enabling the efficient use with multiple ICP-MS instruments. This optimization would lead to more cost reductions.

The use of CO_2 in Ar, supplied from a ballast tank, ensures easy and rapid adjustment of the carbon composition of the plasma with minimal flush out times, addressing a common challenge associated with liquid carbon sources. Carbon was shown to enhance the signal of key elements such as arsenic in the plasma, while maintaining the sensitivity of other elements. The carbon buffering effects of the modified plasma enable the quantification of low concentrations of analytes in food samples, such as grains. Adding carbon to the plasma if especially useful for samples that have variable carbon content, as it compensates for any sample differences and minimizes the variability from easily ionized elements.

Based on our experience, the 8900 ICP-QQQ has proven to be a highly efficient and cost-effective tool for analyzing export grain cargoes, especially in a high-throughput laboratory setting.

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DE29354292

Published in the USA, July 30, 2024
5994-7599EN

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