# Direct Elemental Analysis of Gasoline by Agilent 7500ce ORS ICP-MS

Application

Petrochemical

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## Abstract

**The Agilent 7500ce ICP-MS is shown to be an excellent analytical tool for the elemental analysis of gasoline. It offers the best detection limits of any multi-element technique and a full elemental analysis suite that takes less than 5 minutes to acquire. The Octopole Reaction System (ORS), integral to the 7500ce, ensures that a single method and set of conditions can be used to directly determine all elements of interest in the sample. Comparison data for selected elements in both gas mode and no-gas mode highlight the effectiveness of the ORS for interference removal. Results showing the excellent long-term stability of the 7500ce ORS are also given.**

## Introduction

Traditionally ICP-MS (inductively coupled plasma-mass spectrometry) has not been considered as the most appropriate technique for the measurement of trace metals in organic matrices due to perceived problems with sample introduction, plasma stability, carbon deposition on the interface and lenses, and the formation of carbon-based interferences. These problems can be difficult to overcome without the appropriate hardware setup and methodology, even for the easiest of organic matrices, that is, those with low vapor pressure.

Direct aspiration of gasoline provides a more unique problem due to its relatively high vapor pressure and aggressive nature. The high vapor pressure would typically cause plasma instability, even to the extent that the plasma is extinguished and the aggressive nature of the solvent precludes the use of most types of peristaltic pump tubing.

However, these obstacles are relatively simple to overcome by intelligent system design, choice of sample introduction system hardware, and plasma optimization. The 7500 Series features the only digital drive solid-state plasma RF (radio frequency) generator available in a commercial ICP-MS. The crystal controlled fixed frequency (27.12 MHz) generator features a high-speed real-time matching network maintaining plasma stability when analyzing volatile organic matrices. The 27.12 MHz plasma has been shown to generate a higher ionization temperature than higher frequency plasmas [1], which improves matrix decomposition and also gives lower metal oxide ratios compared to 40.68 MHz plasmas [2].

To help reduce vapor pressure effects on the plasma, the spray chamber must be cooled to improve the condensation of excess solvent vapor produced during nebulization. All 7500 ICP-MS systems feature a Peltier cooled spray chamber that can be set to temperatures below 0 °C, thus reducing the solvent loading on the plasma.  To further reduce the effects of high vapor pressure, a narrow bore torch injector was used (1.0-mm internal diameter (id) in place of the standard 2.5-mm id injector torch). The narrow injector minimizes the effect of solvent droplets rapidly expanding into vapor.

Sample introduction can be facilitated by any solvent-resistant uptake tubing and nebulizer, however, to reduce the likelihood of contamination, avoid Viton uptake pump tubing. In this study, a quartz concentric nebulizer was used under free aspiration to avoid contamination problems.

To eliminate the effects of carbon deposition on the interface and ion lenses, oxygen needs to be introduced into the plasma. For water-soluble solvents, it is often sufficient to dilute the solvent in water as this can provide enough oxygen to convert the carbon into CO or $CO_2$. However for hydrophobic solvents, it is necessary and easier to introduce the solvent directly and add oxygen gas to the plasma. The 7500 can be fitted with an additional mass flow controller that allows the addition of oxygen to the sample stream after the nebulizer and spray chamber. This configuration allows complete control over plasma conditions facilitating easy optimization regardless of the matrix.

### Trace Impurities in Gasoline

The requirement to measure metal impurities in organic matrices varies depending upon the end use. Impurities in gasoline must be controlled to ensure the final quality of the product for example, to ensure reliable burn characteristics. Some metallic impurities, such as vanadium and lead, are catalyst poisons and must be kept under control while other impurities have corrosive properties. Additionally, the metallic impurities must be controlled in order to reduce their environmental impact and meet legislative requirements. The levels and type of impurity also dictate the removal process; some aqueous soluble salts are relatively easy to remove but organic soluble metals (usually porphyrin-metal complexes) are more difficult. An economical approach is often to dilute a product gasoline with high metallic impurities with a cleaner gasoline batch.

### Sample Preparation and Instrumental Conditions

The samples were taken directly from the gas station pump of a leading petroleum company and analyzed using a standard Agilent 7500ce ICP-MS fitted with the Agilent quartz concentric nebulizer and Scott-type double-pass quartz spray chamber; no desolvation device was necessary. Platinum interface cones were used to allow the addition of $O_2$ (as a 50% mix in Ar), which was added after the spray chamber from a separate mass flow controlled channel. The system was fitted with a taper torch with a 1-mm id injector to further improve plasma stability. Instrumental conditions are given in Table 1.

**Table 1. Agilent 7500ce ORS-ICP-MS Operating Conditions**

| Parameter | Value |
|---|---|
| Forward power | 1200 W |
| Plasma gas flow | 15.0 L $min^{-1}$ |
| Auxiliary gas flow | 1.0 L $min^{-1}$ |
| Nebulizer gas flow | 0.70 L $min^{-1}$ |
| Make up gas flow | 0.13 L $min^{-1}$ |
| 50% $O_2$ in Ar flow | 7% open (~0.14 L $min^{-1}$) |
| Sampling depth | 9.0 mm |
| Spray chamber temperature | –5 °C |

All instrumental conditions were optimized from the system's ChemStation PC including all gases, torch position, and sample introduction parameters. The ORS cell gas conditions were essentially identical to those conditions used for aqueous samples, with the exception of a slightly higher hydrogen flow rate (2 mL $min^{-1}$ higher) for the removal of $C_2$ interference on Mg.

Calibration was prepared by weight-weight dilution of the stock standard (Conostan oil-based standards) into the gasoline. Additionally, an internal standard mix (containing Be, Y, In, and Bi) was added to compensate for any sample preparation or minor viscosity differences. The four internal standard elements were added in case any of these elements were present in the sample, thus giving enough flexibility for data processing and method development.

### Data Acquisition

Data was acquired operating the ORS in helium mode [He], hydrogen mode [$H_2$], and no-gas mode [No Gas]. The use of the different gasses generally depends upon the analyte.

Helium is used for the removal of matrix-based interferences regardless of the interference source and is applicable to a single interference-analyte pair, for example, ArC on $^{52}Cr$, as well as the removal of interferences on those masses suffering several different interferences, for example, ArCl, CaCl, ArSH, on As. Because He is inert, no reaction products are formed and polyatomic interferences are removed by energy discrimination (the interfering ion loses more energy compared to the analyte ion and is ejected from the ion beam). He mode is also applicable to reducing argon-oxide, metal-oxide, and metal-halide interferences such as CaO, CeO, CaCl, improving the measurement of Fe, As, and interfered rare earth elements (REE) in complex matrices.

$H_2$ reaction mode is used to remove a small number of very large interferences: $N_2$ and CO on Si, Ar on Ca, $C_2$ on Mg (in gasoline), and $Ar_2$ on Se. These are all large, stable and well known interferences, and with the exception of $C_2$ (in organics), these are all plasma-based.

Switching between ORS modes is automatic within a single acquisition, so there is no need to repeat each sample analysis for each mode. Furthermore, no interference equations are necessary as the appropriate gas mode removes all interferences.

Several interfered elements were also determined without cell gas for comparison of cell performance.

### On-Mass Measurements

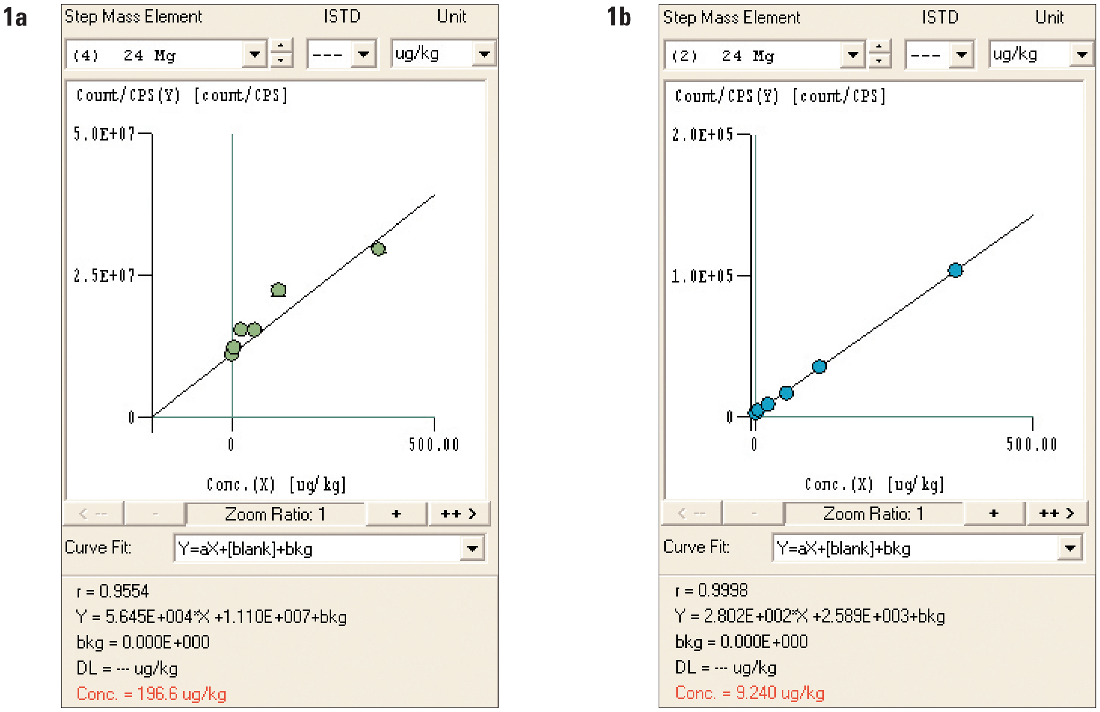
ORS cell mode allows the determination of isotopes that would not normally be available in many sample types. For example the iron 56 isotope ($^{56}Fe$ suffers a severe overlap from ArO and CaO) has higher % relative abundance than the 57 isotope (suffers from ArOH and CaOH interferences), so analyzing the 56 isotope provides better sensitivity and better detection limits (DLs ) once the interferences are eliminated using the ORS cell in He mode.

## Results and Discussion

Table 2 displays the quantitation and DL data for the base gasoline. Notably the effect of the C-based interferences can be observed in the data for Cr and Mg with no cell gas compared to gas mode. The data presented in bold typeface is for information only.

Comparative data has been provided for Cr and Cu in gas and no-gas mode for two free isotopes and also several other elements although during “real-life” analyses, this would not be necessary. Measuring the most abundant isotope in He is the default analysis mode.

Calibrations for several elements are given in Figures 1 to 5. Note the calibrations for Mg (Figure 1a) and Cr (Figure 2a) in no-gas mode; although relatively linear, there is a large offset due to the interferences in the organic matrix ($C_2$ and ArCl, respectively). Figures 1b and 2b show that the respective interferences have been significantly reduced.



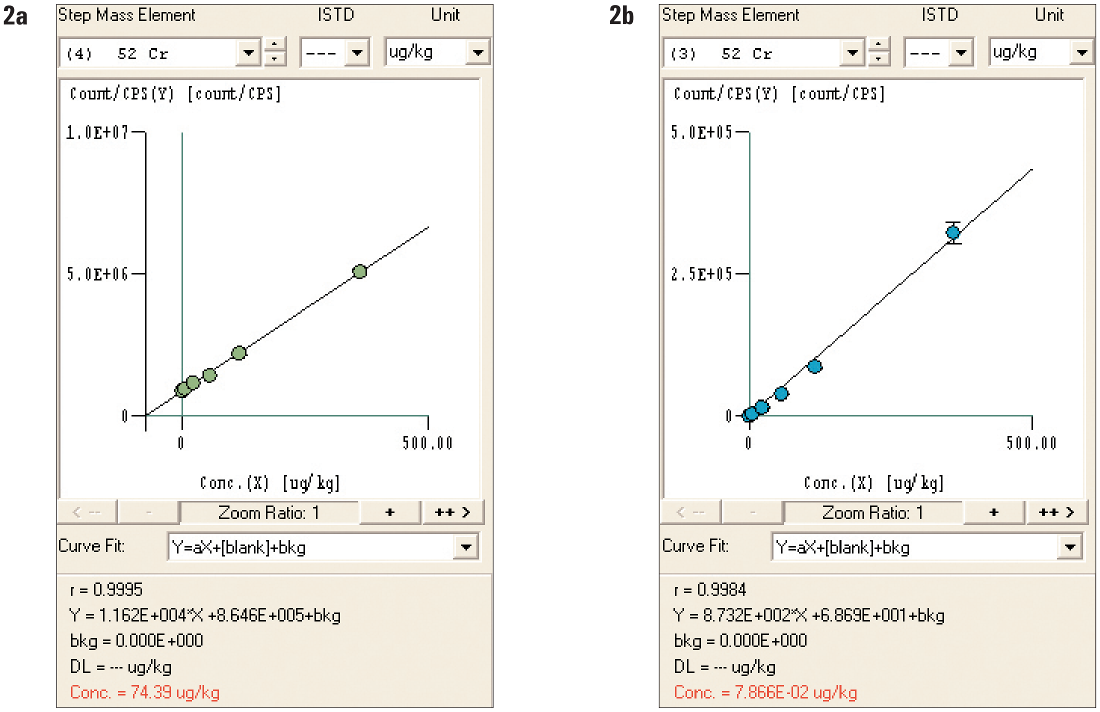
**1a**

Step Mass Element: (4) 24 Mg
ISTD: ---
Unit: ug/kg
Curve Fit: Y=aX+[blank]+bkg
r = 0.9554
Y = 5.645E+004*X +1.110E+007+bkg
bkg = 0.000E+000
DL = --- ug/kg
Conc. = 196.6 ug/kg

**1b**

Step Mass Element: (2) 24 Mg
ISTD: ---
Unit: ug/kg
Curve Fit: Y=aX+[blank]+bkg
r = 0.9998
Y = 2.802E+002*X +2.589E+003+bkg
bkg = 0.000E+000
DL = --- ug/kg
Conc. = 9.240 ug/kg

**Figure 1.** **1a) Magnesium calibration (No-gas mode). Note apparent concentration of 196.6 µg/kg due to $C_2$ interference (left). 1b) Magnesium calibration ($H_2$ Mode). Note concentration of 9.24 µg/kg (right).**


**2a**

Step Mass Element ISTD Unit

(4) 52 Cr --- ug/kg

Curve Fit: Y=aX+[blank]+bkg

r = 0.9995
Y = 1.162E+004*X +8.646E+005+bkg
bkg = 0.000E+000
DL = --- ug/kg
Conc. = 74.39 ug/kg

**2b**

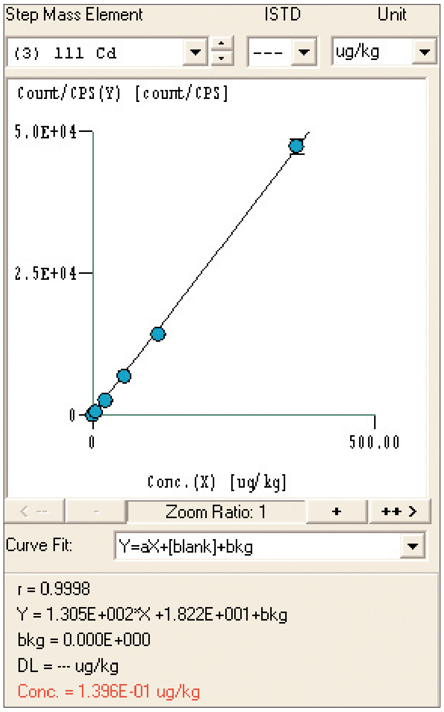
Step Mass Element ISTD Unit

(3) 52 Cr --- ug/kg

Curve Fit: Y=aX+[blank]+bkg

r = 0.9984
Y = 8.732E+002*X +6.869E+001+bkg
bkg = 0.000E+000
DL = --- ug/kg
Conc. = 7.866E-02 ug/kg

**Figure 2.** **2a) Chromium calibration (No-gas mode). Note apparent concentration of 74.4 µg/kg due to Ar C interference. 2b) Chromium calibration (He Mode). Note concentration of 0.078 µg/kg.**

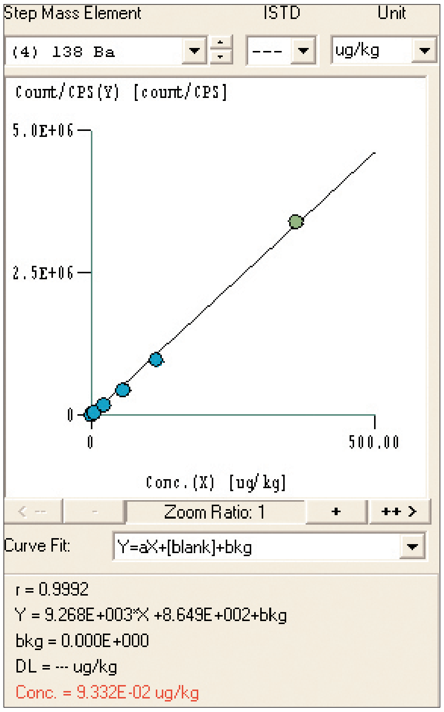

Step Mass Element ISTD Unit

(3) 111 Cd --- ug/kg

Curve Fit: Y=aX+[blank]+bkg

r = 0.9998
Y = 1.305E+002*X +1.822E+001+bkg
bkg = 0.000E+000
DL = --- ug/kg
Conc. = 1.396E-01 ug/kg

**Figure 3.** **Cadmium calibration (He mode).**

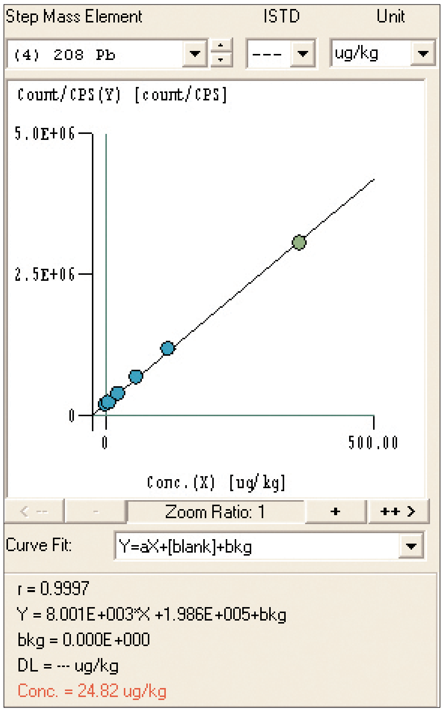

Step Mass Element ISTD Unit

(4) 138 Ba --- ug/kg

Curve Fit: Y=aX+[blank]+bkg

r = 0.9992
Y = 9.268E+003*X +8.649E+002+bkg
bkg = 0.000E+000
DL = --- ug/kg
Conc. = 9.332E-02 ug/kg

**Figure 4.** **Barium calibration (No-gas mode).**



Step Mass Element: (4) 208 Pb
ISTD: ---
Unit: ug/kg
Curve Fit: Y=aX+[blank]+bkg

r = 0.9997
Y = 8.001E+003*X +1.986E+005+bkg
bkg = 0.000E+000
DL = --- ug/kg
Conc. = 24.82 ug/kg

**Figure 5. Lead calibration (No-gas mode).**

It should be noted that the DL data for phosphorus and silicon proved higher than usual in organic matrices due to relatively high concentrations in the base gasoline.

The effect of interferences from the sample matrix can be observed for all the interfered elements in no-gas mode particularly those suffering from carbon-based overlaps. For example, Al suffers from a CN interference while Cr suffers from an ArC interference in no-gas mode; this is borne out in the differences between the quantitation results once a gas is applied to the cell. Data for Cd also improved in He mode, due to the removal of MoO interference on this element.

**Table 2. Quantitation and DL Data for the Gasoline.***

| Element | Mass | Tune | Conc. (µg/kg) | SD | 3σ DL |
|---|---|---|---|---|---|
| B | 11 | $H_2$ | 2.11 | 0.2584 | 0.775 |
| Na | 23 | No gas | 1.57 | 0.009118 | 0.027 |
| Mg | 24 | $H_2$ | 9.24 | 0.08363 | 0.251 |
| **Mg** | **24** | **No gas** | **196.60** | **1.565** | **4.695** |
| Al | 27 | He | 1.36 | 0.2526 | 0.758 |
| **Al** | **27** | **No gas** | **56.86** | **0.1229** | **0.369** |
| Si | 28 | $H_2$ | 316.80 | 10.91 | 32.730 |
| P | 31 | No gas | 310.40 | 0.9064 | 2.719 |
| Ca | 40 | $H_2$ | 5.31 | 0.1445 | 0.434 |
| Ti | 47 | He | 0.18 | 0.1515 | 0.455 |
| V | 51 | He | 0.04 | 0.004013 | 0.012 |
| Cr | 52 | He | 0.08 | 0.001157 | 0.003 |
| **Cr** | **52** | **No gas** | **74.39** | **0.275** | **0.825** |
| Cr | 53 | He | 0.05 | 0.005534 | 0.017 |
| **Cr** | **53** | **No gas** | **32.61** | **1.035** | **3.105** |
| Mn | 55 | He | 0.33 | 0.01104 | 0.033 |
| Fe | 56 | He | 2.85 | 0.03929 | 0.118 |
| **Fe** | **56** | **No gas** | **8.35** | **0.1046** | **0.314** |
| Ni | 60 | He | 0.17 | 0.02741 | 0.082 |
| Cu | 63 | He | 2.10 | 0.04912 | 0.147 |
| Cu | 65 | He | 2.16 | 0.04511 | 0.135 |
| Zn | 66 | He | 12.18 | 0.5757 | 1.727 |
| Mo | 95 | No gas | 1.76 | 0.02916 | 0.087 |
| Ag | 107 | No gas | 1.03 | 0.01434 | 0.043 |
| Cd | 111 | He | 0.14 | 0.03079 | 0.092 |
| **Cd** | **111** | **No gas** | **0.88** | **0.04549** | **0.136** |
| Sn | 118 | No gas | 0.51 | 0.003098 | 0.009 |
| Ba | 138 | No gas | 0.09 | 0.003994 | 0.012 |
| Pb | 208 | No gas | 24.82 | 0.0648 | 0.194 |

*Data was acquired in appropriate cell mode with comparative data for selected interfered elements with no cell gas (shown in bold type) to highlight the incorrect results that would be reported by a non-cell ICP-MS. All data presented as µg/kg.

Note that the data acquired for the elements with more than one isotope (in cell mode) was reproducible. This is a good indication that the cell is efficiently removing matrix and plasma-based interferences.

As He is a totally inert medium, no side reactions can occur which would form interferences in another region of the mass spectrum. In addition helium will not react with analyte ions – it is essentially acting as a simple molecular filter removing all polyatomic interferences.

### Spike Recoveries

There are no commercially available reference materials for inorganic constituents in gasoline so a spike recovery was performed in the sample to test the performance of the method. The % recoveries for this sample are shown in Table 3. Recoveries were very good; although Pb displayed a higher recovery than the other elements, which was probably due to the relatively high concentration already in this sample. P and Si were spiked at a higher concentration due to the higher natural concentration in the sample.

**Table 3. Spike Recoveries in the Gasoline Matrix**

| | **Spike (56.2 µg/kg)** | **% Recovery** |
|---|---|---|
| Na/23 [No gas] | 57.4569 | 102.2 |
| Mg/24 [$H_2$] | 58.435 | 103.9 |
| Al/27 [He] | 55.7417 | 99.2 |
| Ca/40 [$H_2$] | 59.7195 | 106.2 |
| Ti/47 [He] | 59.566 | 106.0 |
| V/51 [He] | 52.5743 | 93.5 |
| Cr/52 [He] | 54.9369 | 97.7 |
| Cr/53 [He] | 55.508 | 98.7 |
| Mn/55 [He] | 56.1541 | 99.9 |
| Fe/56 [He] | 57.075 | 101.5 |
| Ni/60 [He] | 58.916 | 104.8 |
| Cu/63 [He] | 54.745 | 97.4 |
| Cu/65 [He] | 55.647 | 99.0 |
| Zn/66 [He] | 56.38 | 100.3 |
| Mo/95 [No gas] | 50.02 | 89.0 |
| Ag/107 [No gas] | 58.948 | 104.9 |
| Cd/111 [He] | 61.739 | 109.8 |
| Sn/118 [No gas] | 54.4923 | 96.9 |
| Ba/138 [No gas] | 51.775 | 92.1 |
| Pb/208 [No gas] | 67.24 | 119.6 |
| | **Spike (360.82 µg/kg)** | **% Recovery** |
| Si/28 [$H_2$] | 388.39 | 107.6 |
| P/31 [No gas] | 396.62 | 109.9 |

### Instrument Stability

The results show that the 7500ce ORS method is excellent for this sample matrix. However if it were not reproducible or proved to have poor stability over an extended sample batch then the technique would be of less value in a routine environment. To demonstrate the stability of the method a sample was spiked and run continuously for almost 5 hours. Figure 6 displays the recovery for the spiked gasoline sample over the analysis time, normalized to the first repeat. The 7500ce stability proved to be excellent indicating its applicability as a routine technique.

## Conclusions

The results showed that many of the isotopes, which would not normally be available to ICP-MS at trace levels, become readily accessible when using the ORS cell in gas mode. Examples include the removal of all C-based interferences: $^{12}C_2$ on Mg; $^{12}C^{15}N$ on Al; $^{12}C^{16}O$ on $^{28}Si$; $^{40}Ar^{12}C$ on $^{52}Cr$; $^{40}Ar^{13}C$ on $^{53}Cr$ as well as interferences arising from other elemental species: $^{23}Na^{40}Ar$ on $^{63}Cu$; $^{40}Ar^{16}O$ and $^{40}Ca^{16}O$ on $^{56}Fe$; $^{40}Ar^{16}OH$ and $^{40}Ca^{16}OH$ on $^{57}Fe$; $^{32}S^{34}S$ and $^{34}S(^{16}O)_2$ on $^{66}Zn$, and many more potential interferences in variable matrices. Importantly, energy and physical processes govern the interference removal for the majority of interferences with a reactive gas ($H_2$) only being needed for the most intense interferences (Mg, Ca, and Si). This makes setup and operation simple. Method development is quick and easy as only a single set of cell conditions is required, no prior knowledge of the samples is needed, and no interference correction equations need to be set up or updated daily.

## References

1. B. Capelle, J. M. Mermet, J. P. Robin; (1982) *Appl Spectrosc* **36**, 102–106.
2. C. J. Park, K. W. Lee; (1991) *J Anal At Spectrom*; **6**, 431–437.

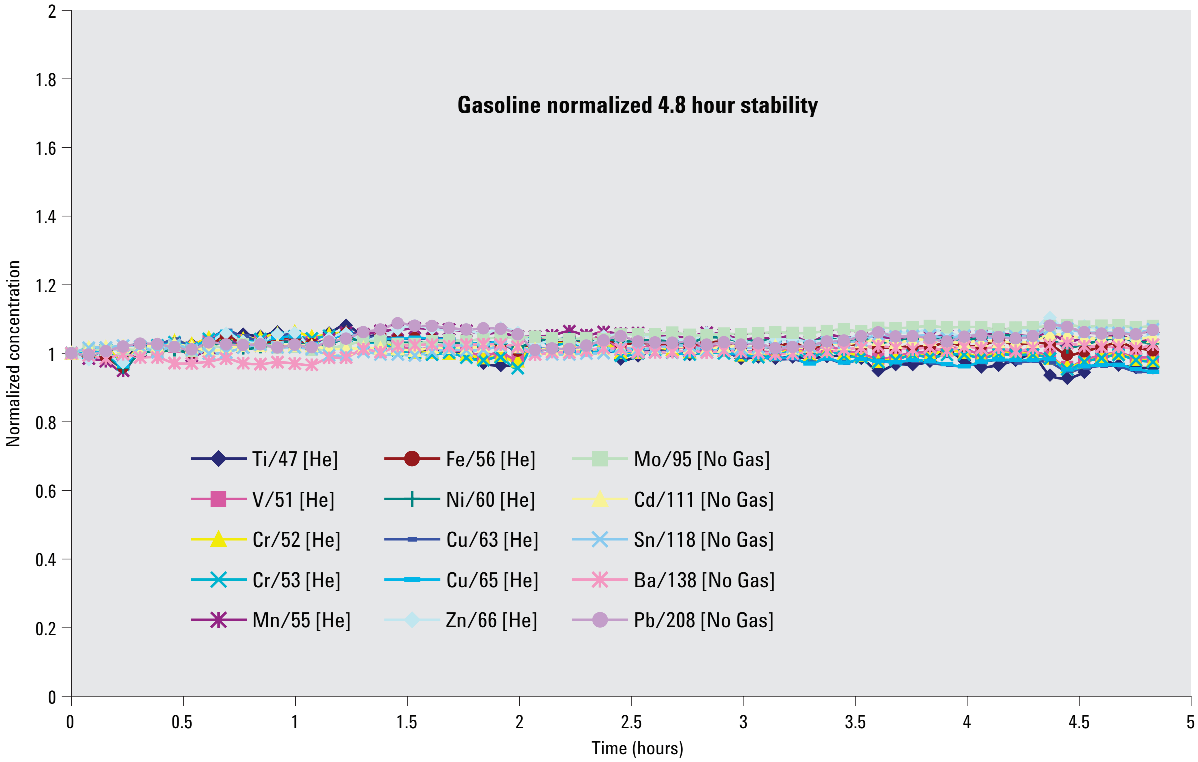


**Figure 6.** **Normalized (to the first analysis) 4.8 hour stability of a continuously aspirated spiked gasoline sample.**

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