

# Multi-elemental determination of gasoline using Agilent 5100 ICP-OES with oxygen injection and a temperature controlled spray chamber

## Application note

Energy & chemicals, petrochemicals

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### Introduction

Trace metals in gasoline are a major source of environmental pollution. They can also adversely affect the performance of automotive engines. Silicon (Si) contamination can be especially problematic as deposits damage components such as catalytic converters and oxygen sensors leading to costly repairs.

ICP-OES is often used for the determination of trace elements in petroleum products due to its reliability, robustness and sensitivity. A successful analysis needs to take account of sample characteristics, such as the high volatility of gasoline. Continuous loading of the plasma with gasoline can affect the stability of the signal and lead to carbon build up on the torch that may cause the plasma to extinguish.



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In this study, the Agilent 5100 Synchronous Vertical Dual View (SVDV) ICP-OES was used for the analysis of 21 elements in gasoline, including Si. Oxygen was added to the auxiliary argon gas flow to reduce carbon build up on the torch, maintain a stable plasma and reduce carbon emission from the organic solvent. A programmable temperature spray chamber, set to -10 °C, was used to reduce vapor loading on the plasma, ensuring a more stable plasma.

### Analysis of volatile organic samples

The 5100 SVDV ICP-OES is highly suited to the analysis of volatile organic samples. It uses a solid state radio frequency (SSRF) system operating at 27 MHz to provide a robust and stable plasma capable of handling a wide range of organic samples, including volatile organics like gasoline. The SSRF has the ability to adjust to rapid changes in the plasma, even when increasing sample uptake speed by fast pumping to 80 rpm. This means that plasma conditions similar to those used for aqueous solutions can be used for organics, without the need for high plasma gas flows.

The sample handling capability of the 5100's vertically-oriented plasma delivers the robustness required for the routine measurement of challenging volatile samples, and ensures maximum plasma stability. The torch is automatically aligned using the simple torch loader and no further adjustments or optical alignments are required. The mechanism also connects all gases for fast startup and reproducible performance.

Depending on established methods and application requirements, the 5100 SVDV ICP-OES can be operated in synchronous vertical dual view (SVDV), vertical dual view (VDV), radial (RV) or axial (AV) modes. As gasoline is traditionally measured radially for better sample handling with a vertical torch, the 5100 was operated in RV mode.

Carbon species present in organic solvents can interfere with some elements. A more accurate measurement of the analyte signal is possible using Agilent's Fast Automated Curve-fitting Technique (FACT) to model the complex background structure due to C-emissions and correct for any spectral interferences [1].

## Experimental

### Instrumentation

The Agilent 5100 SVDV ICP-OES with temperature controlled spray chamber and oxygen injection was used for the determination of 21 elements in gasoline. The instrument was fitted with the volatile organics sample introduction system consisting of a glass concentric nebulizer, 0.8 mm i.d. RV torch, solvent resistant tubing, and an IsoMist temperature controlled spray chamber. The spray chamber was operated at the minimum temperature of -10 °C. An Agilent SPS 4 autosampler was also used.

The 5100 SVDV ICP-OES is equipped with a three port gas module. This allows an Ar/O<sub>2</sub> gas mix to be routed automatically through the auxiliary gas line to prevent carbon build up on the torch, reduce carbon band emissions and sustain the plasma during analysis. The addition of the Ar/O<sub>2</sub> gas mix is fully controlled by the ICP Expert software.

Instrument and method parameters used are listed in Table 1a and b.

**Table 1a.** Agilent 5100 ICP-OES operating parameters

Parameter	Setting
Read time (s)	15
Replicates	3
Sample uptake delay (s)	30 (fast pumping ON)
Stabilization time (s)	10
Rinse time (s)	45
Pump speed (rpm)	10
RF power (W)	1500
Aux flow (L/min)	1.0
Plasma flow (L/min)	12.0
Nebulizer flow (L/min)	0.50
Viewing mode	Radial
Viewing Height (mm)	8
Ar/O <sub>2</sub> addition	Yes
Ar/O <sub>2</sub> (%)	15
Background correction	Fitted and FACT

**Table 1b.** Agilent 5100 ICP-OES sample introduction setup

Parameter	Setting
Nebulizer	Glass SeaSpray
Spray chamber	IsoMist temperature controlled spray chamber
Torch	Volatile organics torch with 0.8 mm ID injector
Sample tubing	Black/Black Solva Flex
Waste tubing	Grey/grey Solva Flex
IsoMist temperature (°C)	-10

### Standards, sample and sample preparation

The method of standard additions (MSA) was used for the analysis to give better accuracy in determining standard and sample concentrations. Complex samples, like gasoline, are difficult to matrix match and must be measured by MSA to minimize physical and chemical differences between samples and standards.

Calibration standards were prepared at 0.5 and 1 ppm by spiking aliquots of gasoline with Agilent A21 oil standard (100 ppm in 75 cSt hydrocarbon oil). Agilent base mineral oil (75 cSt mineral oil) was used to match the viscosity of the standards. The solution was then diluted 1 in 10 using Agilent A-SOLV ICP solvent to give a total oil concentration of 10 % (w/w).

Premium Unleaded Petrol (PULP) 98 Ron was used as the sample. Approx. 2.5 g of the gasoline was diluted 1 in 10 (w/w) in Agilent A-SOLV ICP solvent. The solution was matrix matched using Agilent base mineral oil to give a total oil conc. of 10% (w/w).

To test the recoveries of all 21 elements in gasoline, the samples diluted in Agilent ICP solvent were spiked with low (approx. 0.5 ppm) and high (approx. 1 ppm) concentrations of Agilent A21 oil standard.

### Background correction

In this analysis, Fast Automated Curve-fitting Technique (FACT) correction was applied to P and Pb to minimize spectral interferences from carbon species present in the organic solvent and to improve detection limits. Table 2 displays the Method Detection Limits (MDLs) for P and Pb obtained using Fitted and FACT background correction. The results show that FACT background correction led to lower DLs.

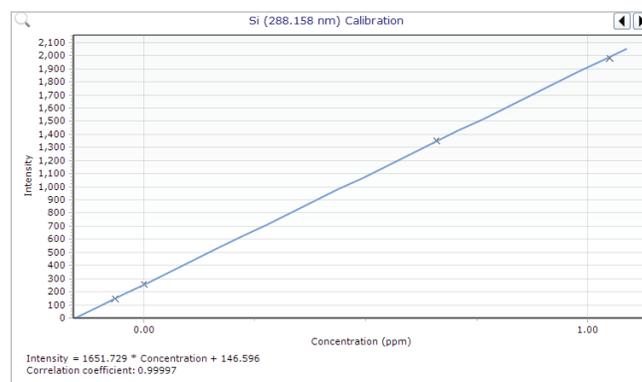
**Table 2.** Method Detection Limits determined using Fitted and FACT background correction techniques

Element and wavelength (nm)	Fitted MDL (ppm)	FACT MDL (ppm)
P 213.618	0.386	0.065
Pb 261.417	1.363	0.119

## Results and discussion

### Calibration linearity

Linear calibrations were obtained for all analytes. Calibration coefficients were greater than 0.999 and the calibration error for each point was less than 10% for all wavelengths. Figure 1 shows the calibration curve for Si 288.158 nm. Table 3 displays the calibration error for each calibration point for 288.158 nm.



**Figure 1.** Calibration curve for Si 288.158 nm shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99997.

**Table 3.** Calibration error (%) for each calibration point for Si 288.158 nm

Standard	Calibration error (%)
Reagent blank	0.00
Addition 1- 0.5ppm	0.91
Addition 2- 1ppm	0.48

MDLs shown in Table 4 are based on three sigma of ten replicate measurements of the blank solution. The replicate measurements were multiplied by 10 to account for the 1 in 10 dilution of the original gasoline sample.

**Table 4.** Method Detection Limits for 21 elements in the original gasoline sample

Element & wavelength (nm)	MDL (ppm)	Element & wavelength (nm)	MDL (ppm)
Ag 328.068	0.020	Mo 281.615	0.058
Al 308.215	0.163	Na 589.592	0.067
B 249.772	0.026	Ni 221.648	0.202
Ba 493.408	0.001	P 213.618	0.065
Ca 396.847	0.008	Pb 261.417	0.144
Cd 226.502	0.018	Si 288.158	0.110
Cr 205.560	0.058	Sn 283.998	0.241
Cu 327.395	0.031	Ti 336.122	0.030
Fe 238.204	0.020	V 311.070	0.014
Mg 285.213	0.021	Zn 213.857	0.024
Mn 257.610	0.004		

**Table 5.** Low and high level spike recoveries for all elements in gasoline

Element & wavelength (nm)	Gasoline sample (ppm)	0.5 ppm spike		1.04 ppm spike	
		Measured conc. (ppm)	Recovery (%)	Measured conc. (ppm)	Recovery (%)
Ag 328.068	<MDL	0.51	103	1.07	103
Al 308.215	<MDL	0.51	103	1.07	103
B 249.772	<MDL	0.53	105	1.09	105
Ba 493.408	<MDL	0.52	103	1.08	104
Ca 396.847	<MDL	0.52	104	1.07	103
Cd 226.502	<MDL	0.50	100	1.04	100
Cr 205.560	<MDL	0.50	100	1.06	102
Cu 327.395	<MDL	0.52	104	1.07	103
Fe 238.204	<MDL	0.51	103	1.06	102
Mg 285.213	<MDL	0.52	104	1.08	104
Mn 257.610	<MDL	0.51	103	1.07	103
Mo 281.615	<MDL	0.51	101	1.06	102
Na 589.592	<MDL	0.54	108	1.09	105
Ni 221.648	<MDL	0.51	103	1.05	101
P 213.618	<MDL	0.49	98	1.02	99
Pb 261.417	<MDL	0.53	106	1.08	104
Si 288.158	0.0117	0.54	108	1.11	107
Sn 283.998	<MDL	0.50	99	1.03	100
Ti 336.122	<MDL	0.52	103	1.07	103
V 311.070	<MDL	0.51	102	1.06	102
Zn 213.857	<MDL	0.50	100	1.03	99

### Spike recoveries

Accuracy was checked by spiking a gasoline sample with two different concentration levels (0.5 and 1.04 ppm). For all analytes, spike recoveries ranged from 98 to 108% (Table 5). The excellent recoveries demonstrate the ability of the 5100 ICP-OES to accurately determine all elements at the required levels in gasoline.

Only Si (0.0117 mg/kg) was detected in the diluted sample with all other elements being below the detection limit for the method.

### Long-term stability

Long term stability (LTS) of the 5100 ICP-OES was measured by continuously analyzing a 1 ppm A21 spiked gasoline sample over an 8 hour period. Over 600 samples were analyzed throughout the entire run, without the need to re-calibrate. The resulting plot for all elements, displayed in Figure 2, shows excellent stability over 8 hours, with recoveries of all elements within  $\pm 10\%$  of target values. Precision (%RSD) was  $< 3\%$  for all spiked elements, as shown in Table 6. These results demonstrate that the combination of the vertical torch and 27 Mhz SSRF system in the 5100 ICP-OES is robust enough to sustain the plasma throughout the 8 hr period of continuous analysis of the spiked gasoline sample. The excellent long term stability achieved is also attributed to the oxygen injected into the auxiliary argon gas flow and the use of the temperature controlled spray chamber to maintain a highly stable plasma.

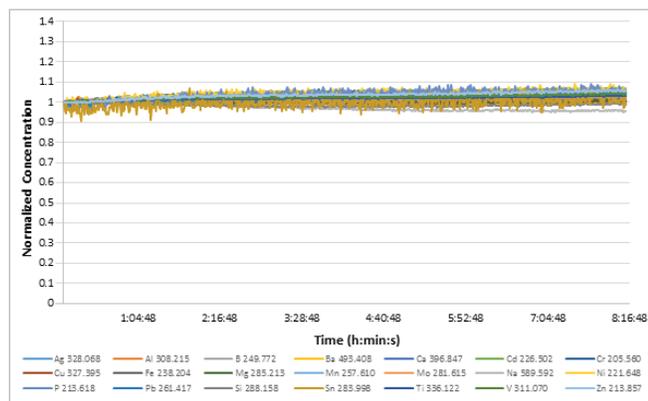


Figure 2. Normalized concentration of 21 elements in spiked gasoline sample

Table 6. LTS results: %RSDs of spiked elements at 1 ppm over 8 hours

Element & wavelength (nm)	%RSD	Element & wavelength (nm)	%RSD
Ag 328.068	0.57	Mo 281.615	1.42
Al 308.215	0.81	Na 589.592	1.57
B 249.772	0.51	Ni 221.648	1.83
Ba 493.408	0.52	P 213.618	2.60
Ca 396.847	0.26	Pb 261.417	1.54
Cd 226.502	1.71	Si 288.158	0.72
Cr 205.560	1.46	Sn 283.998	2.67
Cu 327.395	0.49	Ti 336.122	0.64
Fe 238.204	1.21	V 311.070	0.89
Mg 285.213	0.45	Zn 213.857	1.44
Mn 257.610	1.03		

### Conclusions

Agilent's 5100 SVDV ICP-OES, operating in radial view mode with a vertical torch and 27 MHz SSRF system, provides the stability and robustness required for analysis of volatile organic samples, such as gasoline. With the addition of oxygen and the use of a temperature controlled spray chamber, the 5100 ICP-OES method delivered:

- Excellent method detection limits at sub-ppm levels for all 21 elements
- Excellent spike recoveries in gasoline at 0.5 ppm and 1 ppm level
- Excellent long term stability of 1 ppm spikes in gasoline with  $< 3\%$  RSD drift over 8 hours.

### References

Real-time spectral correction of complex samples using FACT spectral deconvolution software, Agilent publication 5991-4854EN, (2014)

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