Determination of major elements in methanol using the Agilent 4200 MP-AES with External Gas Control Module

Application note

Petrochemical

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Introduction

The conversion of Methanol to Olefins (MTO) is fast gaining momentum as an alternative approach to the production of light olefins (ethylene and propylene) over conventional methods such as naphtha steam and fluid catalytic cracking. Already commercially viable in China, MTO offers low costs of production by utilizing the abundant supply of methanol feedstock produced from natural gas and coal. However, catalysts used during the MTO process are susceptible to deactivation by certain impurities in the methanol feedstock. Major elements such as calcium, potassium, magnesium and sodium present in methanol can interfere with catalytic activity during the MTO process.

Microwave Plasma Atomic Emission Spectrometry (MP-AES) is becoming increasingly popular as a lower cost and safer alternative to Flame Atomic Absorption Spectrometry (FAAS) for multi-elemental analysis of organic samples. For labs handling organic solvents, the presence of the flame of an FAAS is a concern, requiring constant supervision.

The Agilent 4200 MP-AES uses magnetically-coupled microwave energy to generate a robust and stable plasma, capable of the direct measurement of major elements in organic solvents.

Advantages of MP-AES

- Safe technique with low running costs: the microwave plasma is generated using nitrogen gas from a Dewar or a nitrogen generator. This eliminates the need for expensive and/or hazardous gases and allows for unattended operation over long time periods.

- High performance for difficult organic samples: with the use of the External Gas Control Module (EGCM) accessory, air can be added to the plasma to prevent carbon build up and reduce background emissions from carbon species in the plasma.

- Ease of use: intuitive MP Expert software routines and automated hardware features such as the Plug and Play torch simplify instrument set-up and method development.

This application note describes the determination of major elements in methanol using the Agilent 4200 MP-AES fitted with an EGCM accessory.

Experimental

Instrumentation

All measurements were performed using the Agilent 4200 MP-AES fitted with an Agilent Organics Kit comprising the EGCM, OneNeb nebulizer and solvent resistant tubing, in conjunction with the IsoMist programmable temperature controlled spray chamber. By injecting air into the plasma, the EGCM prevents any plasma instability that may arise from the analysis of organic samples by minimizing carbon build up on the torch. It also reduces carbon emissions from the organic solvent leading to increased sensitivity and lower detection limits. As an example, the Instrument Detection Limits (IDLs) in methanol for K 766.491 nm were determined using the 4200 MP-AES with and without the EGCM accessory. The IDLs were found to be 1.23 and 0.24 ppb respectively, showing that lower IDLs are achievable using the EGCM for organic solvents.

The OneNeb inert nebulizer offers high nebulization efficiency of organic solvents and a narrow distribution of small droplets compared to other nebulizers. A cooled spray chamber was used in order to reduce vapor loading on the plasma. Instrument operating parameters and method conditions are listed in Table 1.

Table 1. Agilent 4200 MP-AES operating conditions

Parameter	Value			
Element	Ca	Mg	Na	K
Wavelength (nm)	422.673	285.213	588.995	766.491
Read time (s)	10	5	10	5
Background correction	Off-peak	Auto	Off-peak	Auto
Nebulizer	OneNeb			
Nebulizer flow rate (L/min)	1			
Spray chamber	IsoMist temperature controlled spray chamber			
Spray chamber temp (°C)	0			
Pump rate (rpm)	10			
Sample pump tubing	Orange/Green Organic			
Waste pump tubing	Blue/Blue Organic			
EGCM	On			
Air injection flow rate	High			
Number of replicates	3			
Sample uptake delay (s)	10			
Rinse time (s)	30			
Stabilization time (s)	10			
Gas source	Dewar nitrogen			

Samples and sample preparation

A pre-distillation crude methanol (100% purity) sample obtained from a commercial production process was used for the analysis. The sample was analyzed directly, without any sample preparation.

Multi-elemental calibration standards of Ca, K, Mg and Na were prepared from Agilent 1000 mg/L single element stock solutions at concentrations of 25 ppb, 50 ppb, and 100 ppb. All calibration blanks and standards were prepared using crude methanol as the diluent.

To test for the recovery of Ca, K, Mg and Na in methanol, a sample was spiked with 30 ppb of each elemental standard.

Results and discussion

Working concentration range

All elements showed excellent linearity over the calibrated range with each calibration coefficient being >0.999 (Table 2) and with <10% calibration error for each point for all elements (Table 3). Figure 1 shows the calibration curve for Na 588.995 nm.

Table 2. Wavelength and working calibration concentration range

Element and line (nm)	Concentration Range (ppb)	Concentration coefficient
Ca 422.673	0-100	0.99946
Mg 285.213	0-100	0.99978
Na 588.995	0-100	0.99988
K 766.491	0-100	0.99963

Figure 1. The calibration curve for Na 588.995 nm shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99988.

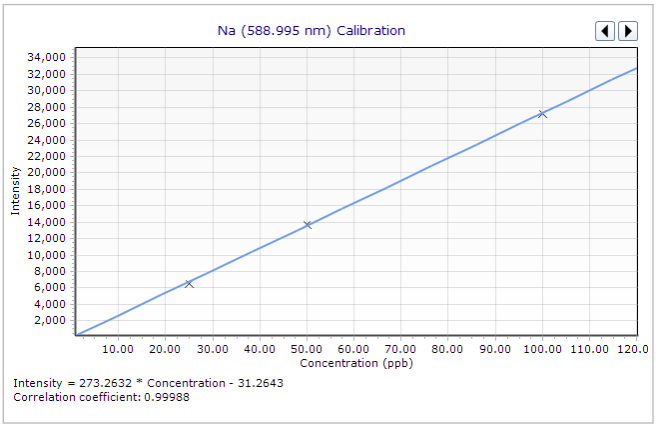

Table 3. Calibration error (%) for each calibration point for Na 588.995 nm

Standards	Calibration error (%)
Blank	0.00
Standard 1- 25 ppb	4.15
Standard 2- 50 ppb	1.11
Standard 3- 100 ppb	0.01

Methods Detection Limits (MDLs)

The MDLs shown in Table 4 are based on three sigma of ten replicate measurements of the 30 ppb spiked sample carried out during the analytical run. An MDL of less than 3 ppb was achieved for each of the four elements analyzed.

Table 4. Element wavelengths and MDLs

Element	Wavelength (nm)	MDL (ppb)
Ca	422.673	1.57
K	766.491	1.35
Mg	285.213	0.93
Na	588.995	2.75

Spike recoveries

To validate the method, ten replicate measurements of the methanol sample, spiked at 30 ppb, were analyzed. This was performed on two instruments, with three determinations on each, for a total of six runs. The plug and play torch was re-loaded on each occasion, to demonstrate the ability of the MP to achieve reproducible results. The average spike recovery for each element was found to be within 97 to 102%, with good precision. The measured values for Ca, Mg, Na, K in methanol were within ±10% of the assigned value. The results are shown in Table 5.

Table 5. Spike recoveries for Ca, K, Mg and Na at 30 ppb in methanol

Element	Ca 422.673	K 766.491	Mg 285.413	Na 588.995
Measured value (mean, n=6, ppb)	29.17	30.16	30.58	30.11
Assigned value (ppb)	30	30	30	30
% RSD	1.79	1.50	1.02	3.05
% Recovery	97	101	102	100

Long term stability (LTS)

The LTS of the Agilent 4200 MP-AES was measured by continuously analyzing the methanol sample, spiked with Na, K, Mg, and Ca at 30 ppb, over a 2 hour period. The resulting stability plot (Figure 2) demonstrates excellent stability (<4% RSD) for all four elements (Table 6).

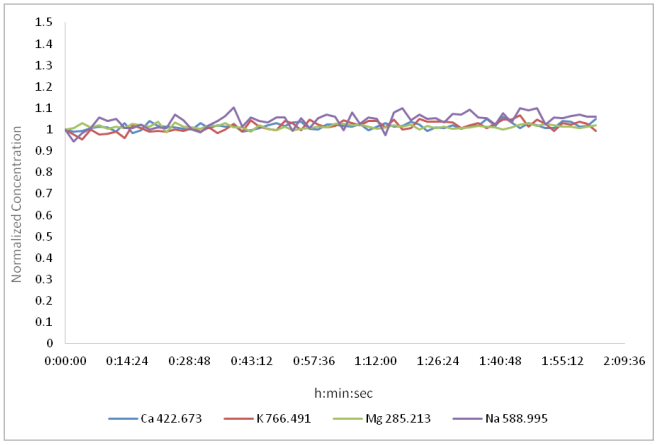

Figure 2. Normalized concentration of Ca, K, Mg and Na in a 30 ppb spiked methanol sample measured over 2 hours.

Table 6. LTS % RSD results for 30 ppb Ca, K, Mg and Na in methanol

Element	Wavelength (nm)	%RSD
Ca	422.673	1.55
K	766.491	2.34
Mg	285.213	1.00
Na	588.995	3.25

Conclusions

The Agilent 4200 MP-AES is highly suited to the analysis of volatile organic solvents. In this study the EGCM accessory and Isomist temperature controlled spray chamber ensured excellent plasma stability, allowing the direct analysis of methanol for Na, K, Ca and Mg at the ppb level. The MP-AES demonstrated:

- High analytical performance with MDLs at single figure ppb level and 30 ppb spike recoveries for all elements within ±10% of the target values.

- Excellent Long Term Stability with %RSD values less than 4% for all four elements.

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Published November 25 2015
Publication number: 5991-6469EN

Agilent Technologies