Investigation of the potential of the 8800 ICP-MS/MS for the quantification of metals in organic solvents and LC-ICP-MS/MS for separation of metal complexes by GPC

Agilent Technologies

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Introduction

In recent years, the petroleum industry has become increasingly interested in the determination of trace and ultra-trace metal levels in crude oil and petroleum products. Established and emerging applications include controlling contamination during refining, monitoring the levels of catalyst poison elements in process streams, using trace element levels, metal porphyrins and other complexes as geochemical biomarkers, and identifying and reducing the sources of atmospheric and environmental pollution from fuels.

Because of its high sensitivity and simple mass spectra, quadrupole ICP-MS (ICP-QMS) is able to achieve sufficiently low detection limits for the elements of interest in the industry. However, the analysis of organic samples by ICP-MS requires a specific sample introduction configuration, and the high carbon and oxygen content in the plasma gives rise to several intense carbon-based polyatomic interferences.

Agilent's 8800 triple quadrupole ICP-MS (ICP-MS/MS) offers a unique capability for interference removal, using controlled reactions in the collision/reaction cell. This provides an interesting alternative to ICP-QMS to solve the polyatomic interferences and achieve lower detection limits and more reliable quantification for key analytes in organic solvents.

Experiments were performed using a sample introduction system adapted for organic samples. Solvent-resistant peri-pump tubings, O_2 addition to the plasma, platinum cones and lower temperature in the spray chamber were used to perform both total metal quantification and LC coupling for the separation of metal-organic aggregates using Gel Permeation Chromatography (GPC), also referred as Size Exclusion Chromatography (SEC).

As the S, V and Ni containing aggregates are targeted to be eliminated as much as possible before hydrocracking processes, the size speciation gives a valuable information on the selectivity of the catalysts used for metal removal in order to improve the refining yield.

Experimental

For the experiments an Agilent 8800 ICP-MS/MS was used in organic configuration hence using:
- 1 mm inner diameter torch
- Platinum skimmer and sample cones
- Addition of O2 to the plasma for carbon decomposition

Determination of the limits of detection was performed in xylene using solvent resistant peri-pump tubing and an ASX-520 auto-sampler. The tuning conditions used are summarized in the table below.

Parameter	Value
RF Power (W)	1550
Sample Depth (mm)	4
Carrier Gas (L/min)	0.35
Make-up Gas (L/min)	0.00
Option Gas (%)	20
O2 cell gas flowrate in MS/MS mode	30 %

For the LC-ICP-MS/MS work, an Agilent 1290 organic solvents compatible HPLC was used. Tetrahydrofuran was used as the preparation solvent for the crude oil and as the mobile phase. The tuning conditions and HPLC conditions are gathered in the table below.

Parameter	Value
RF Power (W)	1550
Sample Depth (mm)	4
Carrier Gas (L/min)	0.23
Make-up Gas (L/min)	0.00
Option Gas (%)	25
O2 cell gas flowrate in MS/MS mode	25 %
THF flowrate (mL/min)	0.7
Injection volume (µL)	20

## Quantification of metals in xylene : Limits of Detection

A multi-element calibration was prepared in xylene and analyze to evaluate the limits of detection. Standard solution were prepared in xylene at $0 - 1 - 5 - 10 - 30 - 60 - 100$ µg/kg using Conostan single element and multi-element standards in oil. For some elements usually measured in Helium mode when using a single quadruple ICP-MS, the measurement was also performed in MS/MS mode using O_2 as a reaction gas.

Limits of Detection in µg/kg

Comparison LoD in Single Quadrupole mode using Helium and in MS/MS mode using O2
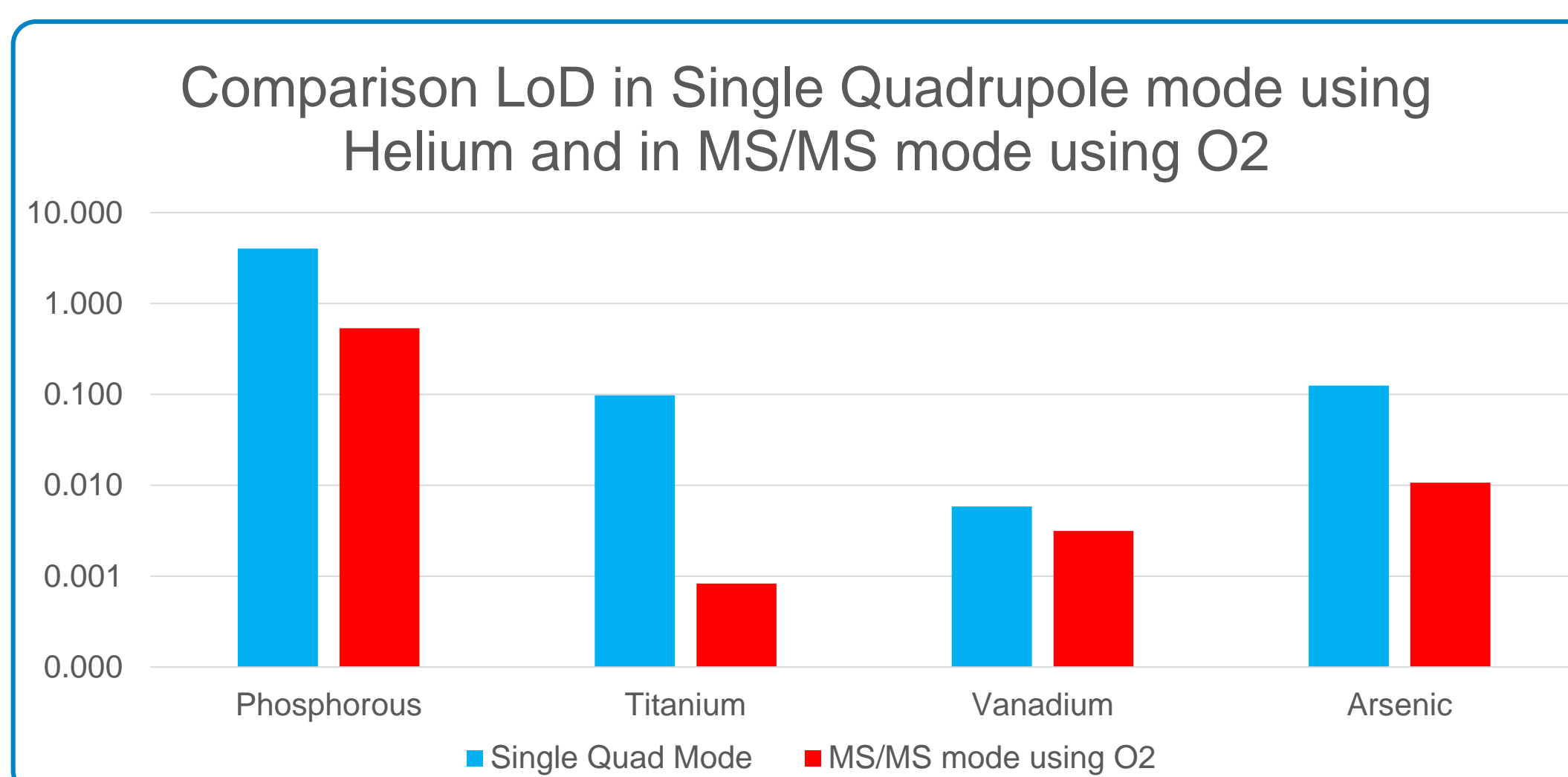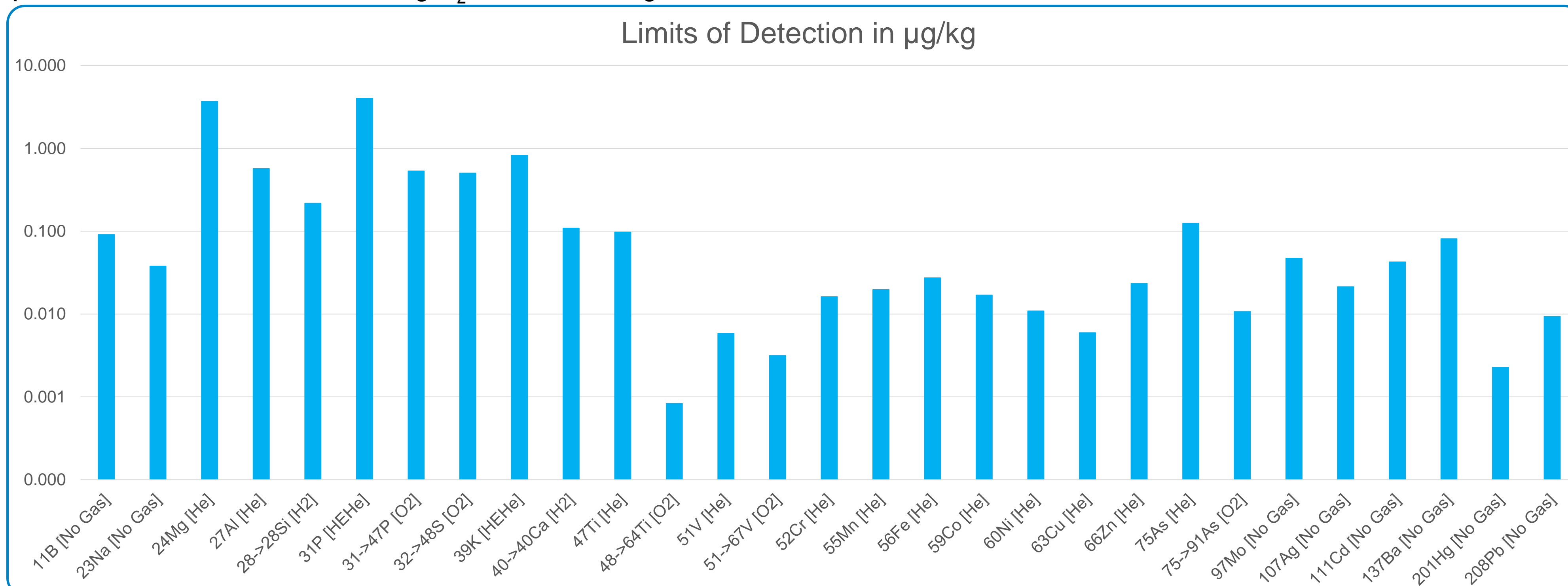
- Detection limits between 0.05 and 0.1 µg/kg for most elements
- Activation of the MS/MS technology with O_2 reaction gas improves by a factor of 10 the LOD on P and As and by a factor of 100 the LOD on Ti
- Sulfur was not detected at 100 µg/kg using Helium in single quadrupole mode
- LOD on sulfur in MS/MS mode using O_2 reaction gas was below 1 µg/kg

$$^{32}S^+ \rightarrow ORC\ (O_2) \rightarrow ^{48}SO^+$$
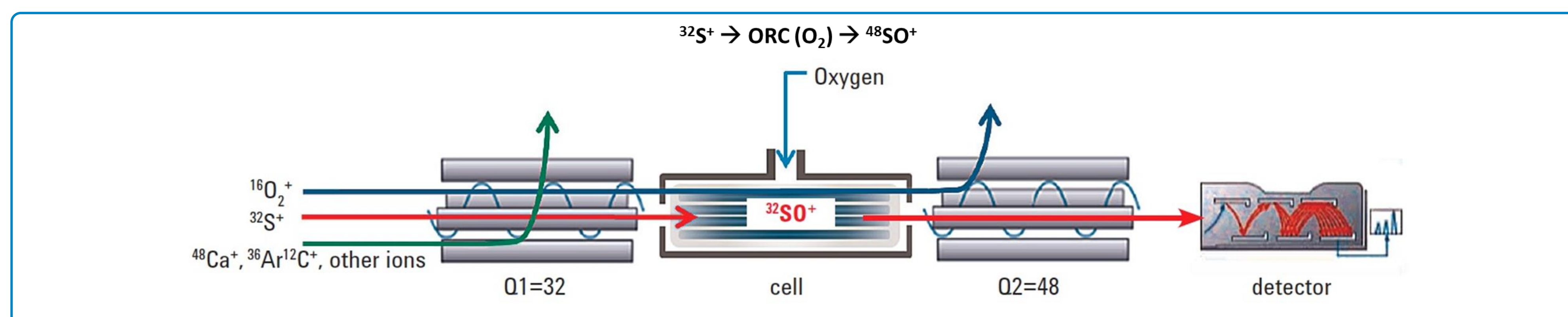
Size distribution of metal-organic aggregates in crude oil using LC-ICP-MS/MS
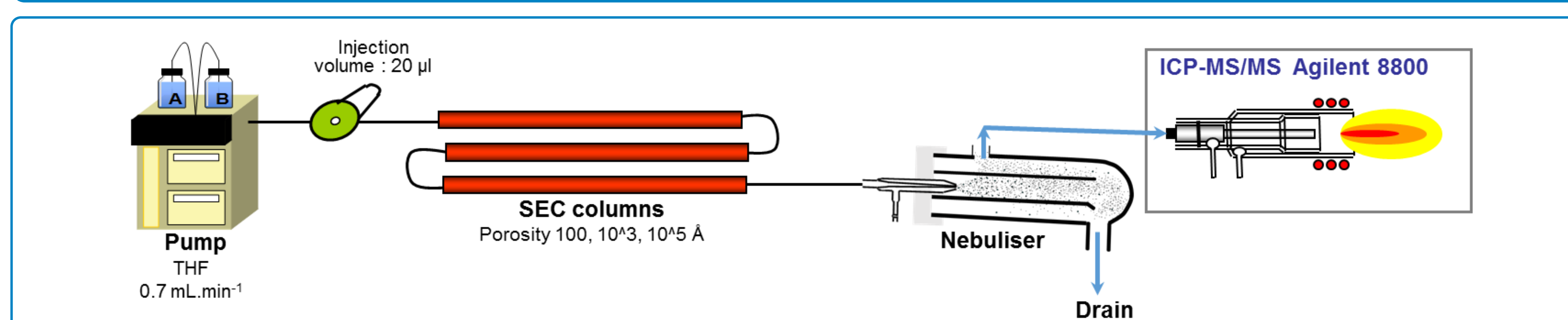
For the LC-ICP-MS/MS experiments, three Agilent GPC columns (PLgelMixed) with increasing porosities were used in series. The flowrate of 0.7 mL/min of THF was directly directed to the ICP-MS/MS through the spray chamber without any prior flowrate splitting. Even with this high organic solvent flowrate, plasma stability remained excellent.

Under the plasma and cell gas conditions described in the experimental section, crude oil samples diluted in xylene were injected. An example of the chromatograms obtained for S, V and Ni are displayed in the figure below.

The profile of the different elements give information on the size distribution of S, Ni or V containing aggregates that occur in petroleum products. Following the evolution of the size distribution over the course of the refining process provides valuable information on the efficiency of the demetallation or cracking catalysts to always improve the refining yield of the crude oil.

Agilent 8800 ICP-MS/MS offers a viable alternative to HR-ICP-MS to study the metal speciation in petroleum products thanks to the unique interference removal capabilities using MS/MS mode with reaction gases.
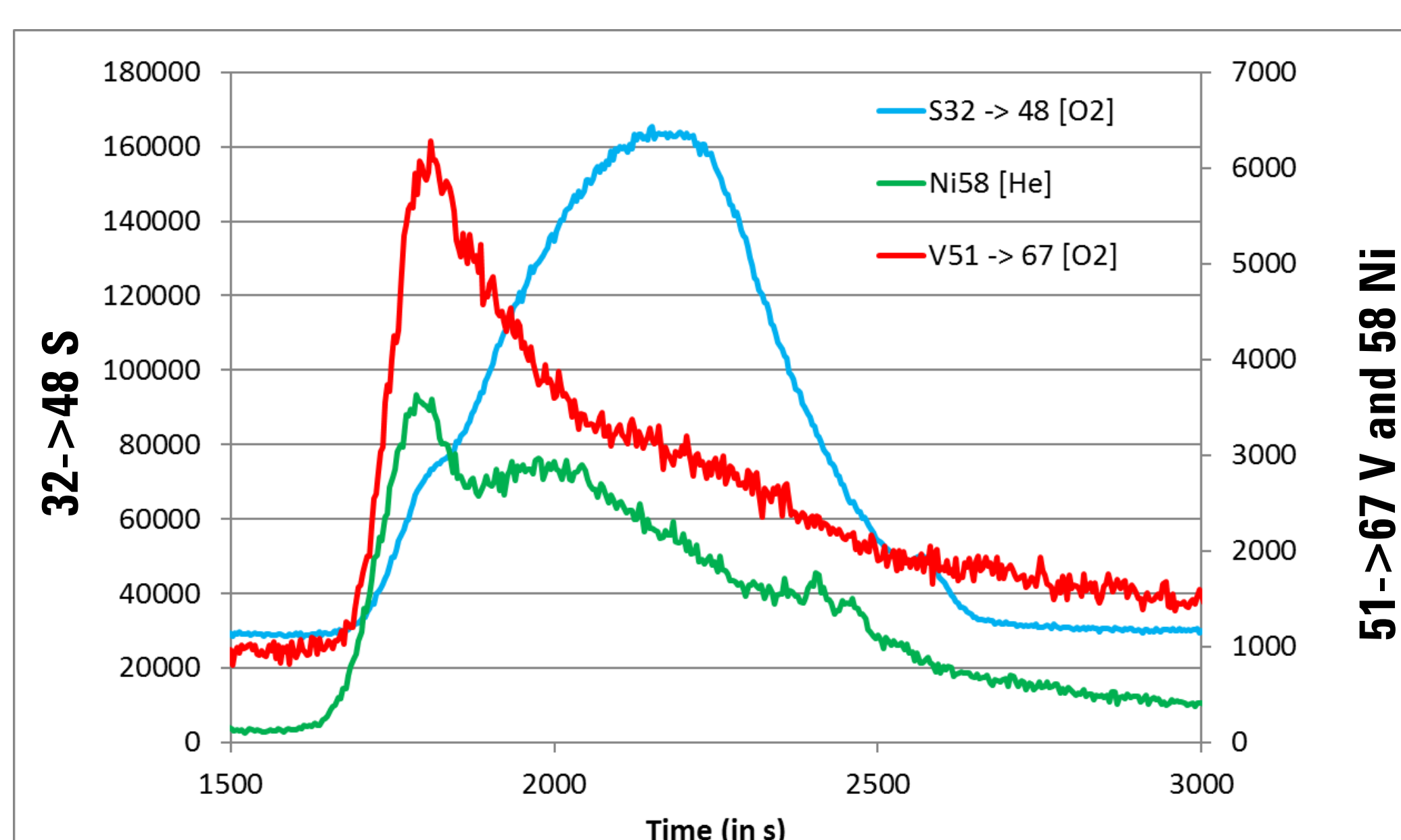
Conclusions

Using Agilent 8800 ICP-MS/MS in organic configuration:
- Excellent detection limits were obtained
- Improved performances were obtained on some difficult elements (S, P, Ti, V and As) using MS/MS mode with O_2 as a cell reaction gas
- Feasibility of LC-ICP-MS/MS coupling in organic mode for the size speciation of metals in petroleum products was demonstrated