

Determination of Chloride in Crude Oils using an Agilent 8900 ICP-QQQ

Fast, accurate analysis of crude oils following direct dilution in an *o*-xylene-based diluent



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Introduction

As stated in a recent study, chlorinated compounds are often removed from crude oil refinery streams (1). To avoid corrosion and fouling during distillation, the concentration of chlorides in crude oil should be less than 1 mg/L. Despite its sensitivity, there are no ASTM standard test methods that use inductively coupled plasma mass spectrometry (ICP-MS) for the measurement of chloride in crude oils. However, ASTM D8110–17 test method specifies ICP-MS for the rapid determination of seven elements in distillate petroleum products (2). Because of its multi-element capabilities, ICP-MS is increasingly used to test petrochemical-based samples for a wide range of elements. It would be convenient to also use ICP-MS for the measurement of chloride.

The determination of chloride in complex matrices is challenging by conventional single quadrupole ICP-QMS. Petroleum crude oil and derivatives may contain sulfur (S), nitrogen (N), and oxygen (O) at variable concentrations, which could promote

multiple interferences in the plasma. The ^{35}Cl isotope (75.8% natural abundance) suffers polyatomic interferences from $^{16}\text{O}^{18}\text{O}^1\text{H}^+$ and $^{34}\text{S}^1\text{H}^+$. Also, Cl is poorly ionized in the plasma because of its high first ionization potential of 12.967 eV, which affects the sensitivity of measurements by ICP-MS. Collision/reaction cells (CRCs) are used successfully to control many common polyatomic interferences in ICP-QMS. However, ICP-QMS cannot reduce the $^{34}\text{S}^1\text{H}^+$ interference sufficiently to allow the accurate determination of Cl at trace levels in samples that contain a high level of S (1).

Experimental

Calibration standard and crude oil sample preparation

The calibration standards were prepared using different concentrations of a Cl organic solvent standard (Conostan, Quebec, Canada) prepared in a diluent. The diluent comprised 90 parts *o*-xylene (Fisher Scientific, NJ, USA) to 10 parts matrix modifier. The matrix modifier was made from mineral oil (80%, Fisher Scientific), a dispersant (20%, Chevron Oronite), and scandium (Sc) and yttrium (Y) spiked at 0.1 mg/kg as internal standards (Conostan, Quebec, Canada). Multiple calibration standards, ranging from 1 to 1000 mg/kg, were prepared by weight. The diluent (90% *o*-xylene to 10% matrix modifier) was run as a blank.

Direct dilution

The composition of the 12 crude oil samples used in this study ranged from C (84 to 89 wt.%), H (10 to 14 wt.%), S (0.3 to 2.5 wt.%), and N (400 to 2500 mg/kg). The samples were diluted 1:5 or 1:10 (using diluent) to allow all Cl concentrations to fit within the calibration range. Standard Reference Material (SRM) NIST 1634c trace elements in fuel oil (Gaithersburg, MD, USA) was prepared at 1:5 and 1:10 dilution. All samples were shaken for two hours in a mechanical shaker. If any residue was seen on the vial walls, a vortex shaker was used to improve sample homogenization.

Instrumentation

An Agilent 8900 ICP-QQQ (#100 for advanced applications) was used. The instrument was equipped with platinum sampling and skimmer cones, a concentric glass nebulizer, quartz spray chamber, and quartz torch with 1 mm injector. The diluted samples were introduced directly into the ICP-QQQ via a peristaltic pump fitted with solvent-resistant tubing (0.89 mm i.d., bought from Cole Parmer). Other parts were from the Agilent Organic Solvent Introduction kit (p/n G3280-60580). An optional gas flow of 20% O_2 in Ar was added to the carrier gas to prevent carbon building up on the interface cones. An *o*-xylene rinse was used between each sample to eliminate any carry-over from the sample introduction system.

Based on the findings of previous studies, hydrogen was used as a reactive cell gas for the determination of $^{35}\text{Cl}^+$ (4, 5). Cl^+ reacts exothermically with H_2 to form HCl^+ , HCl^+ then continues to react via a chain reaction to form ClH_2^+ . This allows the use of the “mass-shift” approach, where the analyte reacts with a reaction gas in the cell to form a product ion, shifting it away from the interference. In this study, Q1 was set to m/z 35 to allow $^{35}\text{Cl}^+$ ions to enter the CRC. The analyte ions then reacted with H_2 in the cell to form $^{35}\text{Cl}^1\text{H}^1\text{H}^+$, while the polyatomic interference ions ($^{16}\text{O}^{18}\text{O}^1\text{H}^+$ and $^{34}\text{S}^1\text{H}^+$) did not react with H_2 . Q2 was set to m/z 37, allowing the product of ion $^{35}\text{ClH}_2^+$ to pass to the detector, free of interference.

ICP-QQQ instrument operating parameters are detailed in Table 1. For comparison purposes, chlorine was also measured using Instrumental Neutron Activation Analysis (INAA), which was carried out by EAI-Elemental Analysis, Inc, an elemental testing facility located in Lexington, KY, USA.

Table 1. ICP-QQQ operating conditions.

Parameter	Value
RF power (W)	1500
Nebulizer gas flow rate (L/min)	0.4
Sampling depth (mm)	8
Spray chamber temp (°C)	-2
Option gas flow rate (mL/min); Ar 80%, O_2 20%	0.35 (35%)
Make up gas flow rate (L/min)	0.1
Nebulizer pump speed (rps)	0.1
H_2 cell gas flow rate (mL/min)	4.6
Octopole bias (V)	-18
Octopole RF (V)	180
Energy discrimination (V)	0
Monitored masses	Q1:35, Q2:37
Integration time (s)	3

Results and discussion

The calibration plot for ^{35}Cl is shown in Figure 1. Three sigma detection limits (DL), limits of quantification (LOQ), and background concentration (BEC) for ^{35}Cl were determined by measuring a blank solution (*o*-xylene diluent containing a matrix modifier and internal standard) ten times. The results are shown in Table 2.

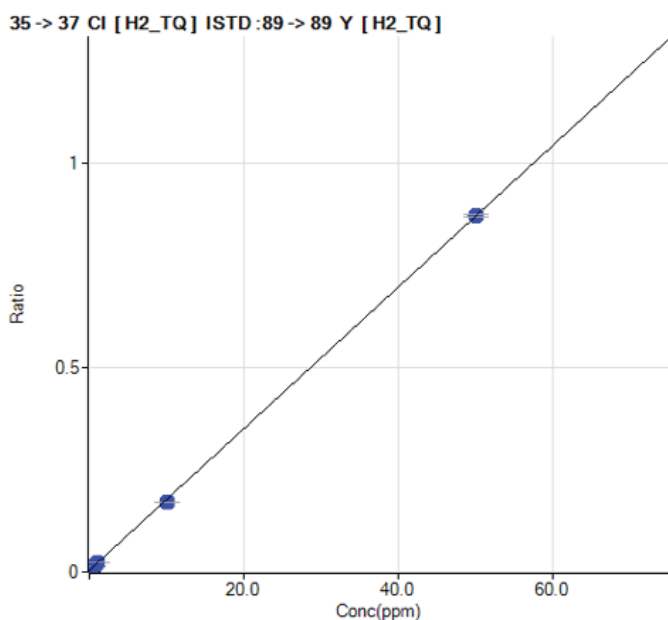


Figure 1. Calibration plot of Cl in *o*-xylene. Units: mg/kg (ppm).

Table 2. DL, LOQ, and BEC of ^{35}Cl in a blank solution determined by ICP-QQQ in H_2 mass-shift mode.

	Detection Limit (mg/kg)	LOQ (mg/kg)	BEC (mg/kg)
^{35}Cl	0.01	0.04	0.24

Reference material analysis

Chlorine was determined in the petroleum feedstock SRM using the 8900 ICP-QQQ operating in H_2 mass-shift mode. The reference value for chlorine in NIST 1634c is 45 mg/kg. The SRM was diluted in *o*-xylene at two different dilution factors. Other than carbon and hydrogen, real petroleum samples contain heteroatoms, S, N, and O, and metals such as V and Ni, among others. The sulfur content of NIST 1634c is around 2 wt.%, so the SRM is a useful test sample for ICP-QQQ given the likely interference on ^{35}Cl by $^{34}\text{S}^1\text{H}^+$. As can be seen from the results presented in Table 3, excellent recoveries were obtained for ^{35}Cl , irrespective of the dilution factor ($100 \pm 10\%$). Since H_2 effectively reacts with Cl^+ to form ClH_2^+ , the interferences on ^{35}Cl can be avoided by measuring the product ion $^{35}\text{ClH}_2^+$ at m/z 37.

Table 3. Determination of Cl concentration in NIST 1634c SRM in *o*-xylene diluent using ICP-QQQ.

	Dilution Factor 5		Dilution Factor 10	
	Concentration (mg/kg)	*Recovery (%)	Concentration (mg/kg)	*Recovery (%)
^{35}Cl	44.33 ± 1.00	99	48.28 ± 1.89	107

*NIST reference value for Cl = 45 mg/kg, S = 2 wt%

Quantitative analysis of crude oil samples

Twelve petroleum crude oil samples with a sulfur content spanning from 0.38 up to 2.01 wt.% and hydrogen to carbon (H/C) ratio from 1.68 to 1.88 were analyzed by ICP-QQQ. The H/C provides an insight to the aromatic/paraffinic nature of the crude samples, which has implications for trading, processing, and stability of crude. The quantitative results for Cl measurements are given in Table 4.

Table 4. Determination of the Cl concentrations in 12 petroleum crude oil samples in *o*-xylene diluent using ICP-QQQ operating in H_2 mass-shift mode. Dilution factor 1:5. n = 3.

Sample	S (%)	H/C	^{35}Cl Measured Concentration (mg/kg)	Sample	S (%)	H/C	^{35}Cl Measured Concentration (mg/kg)
S1	0.38	1.84	22.32 ± 0.36	S7	1.19	1.78	24.80 ± 1.04
S2	0.38	1.85	12.80 ± 0.07	S8	1.19	1.78	20.78 ± 0.08
S3	0.38	1.86	22.84 ± 0.16	S9	1.97	1.71	48.33 ± 2.38
S4	0.38	1.88	6.15 ± 0.05	S10	1.99	1.68	18.25 ± 0.24
S5	0.50	1.85	33.89 ± 0.31	S11	2.01	1.70	50.35 ± 3.00
S6	0.59	1.87	24.87 ± 0.15	S12	2.01	1.71	17.68 ± 0.55

Comparison of results

To further evaluate the accuracy of the ICP-QQQ method, quantitative results for Cl were compared with the results obtained by INAA. The results obtained for three crude samples are shown in Table 5.

Table 5. Comparison of measured Cl concentrations in crude oil samples obtained by ICP-QQQ (dilution factor 1:5) and INAA.

Sample	Measured Cl Concentration (mg/kg)	
	ICP-QQQ	INAA
S2	12.80 ± 0.07	14.40 ± 0.59
S4	6.19 ± 0.05	12.90 ± 0.53
S5	33.89 ± 0.31	25.30 ± 0.91

Depending on the sample, the agreement between the results obtained by ICP-QQQ and INAA was reasonably close. The agreement for sample S2 was around 89%, whereas it was slightly higher at 134% for sample S5. A similar observation was reported recently for these types of samples, using the same techniques (6). The low bias of the ICP-QQQ result for sample S4 suggests that the sample may contain solids or is heterogeneous. A qualitative XRF analysis of S4 suggested the presence of solids (most likely NaCl), which would explain why the ICP-QQQ result was low. It is likely that S4 wasn't fully solubilized or well dispersed in the *o*-xylene diluent.

Conclusion

The Agilent 8900 ICP-QQQ is suitable for the determination of chlorine in petroleum crude samples. Despite the complex matrix, potential interferences on Cl ions originating from the crude petroleum samples were handled effectively using MS/MS technology. MS/MS enables more consistent and reliable reaction gas methods to be used for difficult elements, such as chlorine in complex matrices, than single quadrupole ICP-MS.

In this study, a BEC of 240 µg/kg was achieved for the most abundant Cl isotope, $^{35}\text{Cl}^+$, using mass-shift mode and H_2 cell gas. Interferences from $^{16}\text{O}^{18}\text{O}^1\text{H}^+$ and $^{34}\text{S}^1\text{H}^+$ on $^{35}\text{Cl}^+$ were avoided by measuring the product ion $^{35}\text{ClH}_2^+$ at m/z 37.

A NIST trace element in fuel oil SRM and 12 crude oil samples were prepared for analysis using direct dilution. The specially prepared diluent contained *o*-xylene and a mineral oil matrix modifier, a dispersant, and internal standards. Excellent recoveries of Cl (99 and 107%) in the SRM were determined at two different dilution factors (5 and 10).

The petroleum crude samples were analyzed using ICP-QQQ, and some of the results were checked using INAA. The results show the importance of fully solubilized samples when using direct dilution as the sample preparation technique to avoid biased results due to the presence of particles.

Chloride was measured above the potential-corrosion trigger threshold of 1 mg/L in all 12 crude oil samples, indicating a risk of corrosion at refining facilities from the formation of HCl.

References

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More information

For a full account of the method development, see Jenny Nelson, Laura Poirier, and Francisco Lopez-Linares, Determination of Chloride in Crude Oils by Direct Dilution using Inductively Coupled Plasma Tandem Mass Spectrometry (ICP-MS/MS), *J. Anal. At. Spectrom.*, **2019**, Advance Article, DOI 10.1039/C9JA00096H

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