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1 Determination of chloride in crude oil using isotope dilution GC-MS: a

2 comparative study

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12 Graphic abstract



- Matrix free HS GC-MS analytical method for Cl⁻ quantitation in crude oils is proposed
- The method enables high sample throughput with low maintenance cost
- High precision and accuracy of method is achieved by isotope dilution
- Validation of HS GC-MS method showed good agreement with CIC and ASTM D3230
- 20

21 Keywords:

22 crude oil, inorganic chloride, GC-MS, isotope dilution, ion chromatography

24 Abstract

Optimisation and validation of a novel isotope dilution gas chromatography mass spectrometry 25 (GC-MS) method for determination of inorganic chloride (Cl⁻) in crude oils is presented. The use 26 27 of stable isotope dilution calibration approach decreases losses and biases and it is considered a higher order measurement approach. Samples were diluted with a 1:1 blend of isopropyl 28 alcohol: toluene with 5% water, mixed with ³⁷Cl⁻ internal standard, water extracted and derivatized 29 with triethyloxonium tetrafluoroborate at room temperature. This reagent converted Cl⁻ into stable 30 31 ethyl chloride (EtCl) which was detected by headspace GC-MS. A limit of quantitation of 100 µg kg⁻¹ and limit of detection of 30 µg kg⁻¹ were observed in crude oil samples when initial dilution 32 was not required. The performance of this novel method was compared with combustion ion 33 34 chromatography, ion chromatography with conductivity detection after microwave-induced 35 combustion, and ASTM D3230 method on a set of medium and heavy crude oil samples. A reasonable level of agreement was observed considering the differences in measure and 36 37 definitions and the complexity of the crude samples where Cl⁻ ranged from 0.38 ± 0.02 to $993 \pm$ 103 mg kg⁻¹. This headspace GC-MS method proved to be suitable for analysis of all types of 38 39 crude oils samples with an excellent reproducibility (RSD <6%) and high sample throughput (7 min GC-MS run time). 40

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43 **1.** Introduction

Crude oils contain large variety of elements, some of them are benign for industrial applications, whereas others could have negative impact during regular operations. Among them, inorganic salts, mostly found as chlorides (Cl⁻), belong to the latter group and can be present in appreciable quantities. Within the oil refinery process, Cl⁻ can readily hydrolyze to HCl gas which, upon contact with moisture, forms corrosive aqueous HCl [1]. If this reaction takes place in a high temperature and pressure equipment, the corrosion initiated by HCl can have a detrimental impact
on the crude oil refining facilities [2, 3].

In attempts to reduce the concentration of CI^- , crude oils are being desalted by washing with water [2, 4]. However, the efficiency of this procedure is matrix dependant and its efficacy is reduced when heavier fractions are processed [1]. While optimization of the desalting process could reduce residual CI^- , accurate knowledge of its concentration present in the feed before and after desalting is required for process control. Quantitation of total Cl in crude oils is not a trivial task and narrowing it down to specific chemical species (i.e. CI^-) is a great analytical challenge.

57 When it comes to crude oil analysis, the complexity of the sample matrix is the first obstacle for the design of an analytical method. In fact, crude oil is a complex mixture of 58 hydrocarbon compounds that can be grouped in four main classes based on solubility and 59 polarizability: saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes. 60 61 Chemical composition of crude oils determines its density, viscosity, flash point and adhesion. Saturated hydrocarbons are dominant in light crude oils, which are of a low density, viscosity, 62 63 flash point and adhesion, whereas heavy crudes are rich in resins and asphaltenes [5]. Due to such potential matrix heterogeneity, one can expect that in certain crude oils the Cl⁻ distribution 64 65 would be non-homogenous. Chlorides can be present in aqueous micro-droplets dispersed within crude oil matrix or as a crystalline salt encapsulated in waxes [2]. When analyzed in light crude 66 oils, Cl⁻ can easily sediment, while in viscous samples it might be problematic to achieve 67 homogeneity. Similarly, quantitative aqueous extraction of Cl⁻ from heavy crude oils is often 68 69 hindered by formation of stable emulsions which are very difficult to break [6]. Thus the performance of analytical methods which require Cl⁻ extraction from crude oils [7-10] will be matrix 70 dependent. 71

With regards to instrumentation, very often the matrix complexity of crude oils poses remarkable limitations to the application of current analytical technology. Sample homogeneity can be particularly challenging if a small sample volume is required for the analysis. Combustion

ion chromatography (CIC) takes between 40 and 80 mg of crude oil, what could result in bias 75 76 caused by unrepresentative sampling. Depending of the type of reservoir, production method and type of crude oil, it can contain multiphase solutions with particulates and emulsions which can 77 undergo phase separation during the measurement. Sedimentation of CI⁻ can result in variability 78 79 between repeated measurements of the same sample when the measurement response is based on optical properties of the sample such as X-ray fluorescence spectrometry (XRF) or when 80 samples are let to sit in an autosampler [11]. Chemical constituents of crude oils can cause 81 82 several interferences when analyzed by spectrometric instruments. Polyatomic interferences $({}^{16}O^{18}O^{1}H^{+}, {}^{34}S^{1}H^{+} at {}^{35}CI^{+} and {}^{36}Ar^{1}H^{+}, {}^{36}S^{1}H^{+} at {}^{37}CI^{+})$ generated by ionisation of crude oil matrix 83 in inductively coupled plasma (ICP) are particularly difficult to eliminate in mass spectrometry 84 (MS) [12], more notorious in crude oil with sulfur content above 2 wt.% [11]. Similarly, X-ray 85 excitation beam in XRF is matrix dependent and therefore the response can significantly vary 86 87 between samples and calibration standards [13].

In order to overcome most of the problems of current analytical procedures, we recently 88 developed a headspace gas chromatography mass spectrometry (HS GC-MS) method for 89 quantitation of Cl⁻ in fuel oil [14]. This approach was based on a simple single step derivatization 90 91 with triethyloxonium tetrafluoroborate [15, 16] which allowed the conversion of Cl⁻ into volatile EtCl, readily separated from the complex matrix and detected by HS GC-MS. High-precision 92 quantitation was achieved by isotope dilution (ID) using ³⁷Cl enriched Cl⁻ as internal standard [17] 93 and quantitative Cl⁻ recovery was obtained on the NIST SRM 1634c standard. In this study, the 94 95 scope of HS GC-MS method was further extended for a broad spectrum of crude oils samples including medium and heavy crude oils. The method performance was compared with combustion 96 ion chromatography analysis (CIC) routinely used in many laboratories, microwave-induced 97 98 combustion ion chromatography, and the industrial standard method ASTM D3230 (electrometric 99 analysis).

101 **2.** Materials and methods

102 2.1 Reagents, standards and samples

Sodium chloride (NaCl, 99.5%), anhydrous 2-propanol (i-PrOH, ACS grade), acetonitrile 103 104 (MeCN, HPLC grade), sodium bicarbonate solution (0.1 M NaHCO₃), sodium carbonate solution 105 (0.1 M Na₂CO₃), chloride aqueous standard (1000 \pm 4 mg kg⁻¹ Cl⁻), and triethyloxonium tetrafluoroborate (Et₃OBF₄, 97%) were purchased from Sigma-Aldrich (Oakville, ON, Canada). A 106 solution of Et₃OBF₄ was prepared by mixing 1 g Et₃OBF₄ with 1 mL of acetonitrile (MeCN) pre-107 cooled at -20 °C. Such solution was stable at -20 °C for over a month; before disposal, the 108 109 Et₃OBF₄: MeCN solution was hydrolyzed in water. Toluene (C₇H₈, ACS grade), methanol (reagent grade), 1-butanol (reagent grade), xylene (reagent grade) and hexane (reagent grade) were 110 obtained from Fisher Scientific (Napean, ON, Canada). Solvents were anhydrous as reported 111 112 from manufacturer and used without further purification. Isotopically enriched solution of ³⁷Cl⁻ 113 ERM-AE642 (164.6 mg kg⁻¹ Cl⁻) was purchased from Joint Research Center, Geel, Belgium, whereas the NIST SRM 1634c was sourced from the National Institute of Standards and 114 115 Technology (Gaithersburg, MA, USA). All preparations and dilutions were done gravimetrically. The 1:1 vol mixture of *i*-PrOH:C₇H₈ with 5% of water was used for sample dilution and for the 116 117 preparation of the internal standard solution: 12 mg kg⁻¹ ³⁷Cl⁻ [14]. Ultrapure water was obtained in house with a Thermo Scientific Gen-Pure UV xCAD plus system (18.2 M Ω cm at 25 °C). 118

Twenty one crude oil samples of varying physical and chemical properties were analyzed.
Samples S1-S11 were medium to light crude oils of following properties: API° 30-45; C 85-87
wt.%; H 11-13 wt.%; S 3000 -25000 mg kg⁻¹; N 400-2500 mg kg⁻¹. Samples S12-S21 were heavy
crude oils; however, unknown elemental composition.

123

124 2.2 Sample preparation and instrumentation

125 2.2.1 GC-MS analysis.

126 Prior to sub-sampling, all crude samples were heated in a hot block to 60 °C for 30 min 127 and vortexed for 5 min to improve homogeneity. Samples of high viscosity or high Cl⁻ content were diluted in *i*-PrOH:C₇H₈ with 5% water in 1:5 ratio. Accurately weighted 1.0 mL of sample was 128 129 transferred into clean glass vial and mixed with ³⁷Cl⁻ internal standard (IS) prepared according to 130 previously published method [14]. Following 15 min equilibration during vortex mixing, 1 mL of water was added, and samples were mixed on vertical shaker for additional 15 min at 500 rpm. 131 Subsequently, samples were centrifuged at 2000 x g for 5 min, aqueous phase was transferred 132 into a 10 mL headspace vial and derivatized with 50 µL of Et₃OBF₄ solution [14]. All calibration 133 134 standards were prepared in water. Prior to analysis, 1 mL of standard was transferred into a 10 mL headspace vial and mixed with ³⁷Cl⁻ IS. After 15 min equilibration, this blend was derivatized 135 with Et₃OBF₄ solution. All samples and calibration blends were then analyzed by HS GC-MS. 136

137 An Agilent 7000 TripleQuad GC-MS with a CTC PAL3 autosampler was used in EI mode 138 for detection of EtCl in the headspace. The vials were incubated for 12 s at 40 °C and 0.75 mL of headspace was sampled and injected in the GC inlet. The syringe was kept at 70 °C and flushed 139 for 3 min with N_2 after injection. A split liner (1 mm ID x 6.3 mm OD x 78.5 mm length) was held 140 at 120 °C. The injection was performed with a 1:10 split ratio. A 7 min of isotherm at 30 °C 141 (constant He flow: 1 mL min⁻¹) was sufficient to elute all major compounds from the DB-1701 142 column (30 m length x 0.250 mm ID x 0.25 µm film). The transfer line was set at 220 °C. On this 143 program, the EtCl derivative eluted at 1.6 min separated from the peak of air which was bypassed 144 with a 1.45 min solvent delay. The mass spectrometry detection was performed in selective ion 145 monitoring (SIM) mode by monitoring two ions with a dwell time of 50 ms each: m/z 64 for Et³⁵Cl⁺ 146 and 66 for Et³⁷Cl⁺. Temperature of the MS source and guadrupoles was 150 °C. Detection was 147 obtained on a gain factor of 5. 148

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150 2.2.2 CIC analysis.

151 All samples, except S-21, as received were homogenized by shaking in an automatic 152 shaker for 1 minute. Since S-21 was heavy crude oil sample, it was homogenized by heating in a 153 hot block at 60 °C for 30 min and vortexed for 1 minute. Accurately weighted (40 – 80 mg) sample 154 was placed on the autosampler boat and analyzed by CIC setup without any pre-treatment. 155 Samples of high CI concentration (total chloride concentration > 100 mg kg⁻¹) were diluted with ultrapure toluene, ensuring that the reading would fit the calibration curve. A set of eight mineral 156 oil chloride standards (purchased from Conostan) were used for calibration in a range of 0 – 100 157 mg kg⁻¹. The neat standards and samples were placed in the autosampler, and the analysis was 158 run according to specifications in Table 1.Combustion module was kept at 1050 °C with 159 continuous supply of O₂ (300 mL min⁻¹) and Ar (100 mL min⁻¹). All columns were kept at 30 °C. A 160 set of two CI standards (Conostan SCP) at concentrations of 3 and 10 mg kg⁻¹ was used for quality 161 162 assurance with calculated recoveries within 5% of the certified value.

163

164 Table 1. Instrumental parameters of combustion ion chromatography using 930 Compact IC Flex with 165 conductivity detector (Metrohm AG) and ion chromatography 850 Professional IC.

	Metrohm 930 Compact IC Flex	Metrohm 850 Professional IC
Column	Metrosep A Supp 5 - 150/4.0	Metrosep A Supp 5 – 240/4.0
	Metrosep A Supp 4/5 Guard/4.0	Metrosep A Supp 4/5 Guard/4.0
	Metrosep A PCC 1 HC/4.0	
Mobile phase A	3.2 mM sodium carbonate	3.2 mM sodium carbonate
Mobile phase B	1.0 mM sodium bicarbonate	1.0 mM sodium bicarbonate
Eluent Flow Rate	0.7 mL min ⁻¹	0.7 mL min ⁻¹
Suppressor regenerate	0.5 M sulfuric acid	0.5 M sulfuric acid
Rinsing solution	Ultrapure water	Ultrapure water
Absorption solution	300 mg L ⁻¹ hydrogen peroxide	

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8 2.2.3 *Microwave-induced combustion ion chromatography (MIC-IC).*

Sample preparation was performed by microwave-induced combustion (MIC) following a 169 previously published method for chlorine analysis in heavy crude oil [18]. Briefly, 100 to 150 mg 170 of crude oil was wrapped into polyethylene. Graphite (25 mg) was added as a flame retardant to 171 172 control the kinetics of the combustion reaction to samples, based on a method reported for diesel oil [19]. Ammonium nitrate (50 % m/v, 50 µL) was used as igniter and ammonium hydroxide (100 173 mM, 6 mL) was used as absorbing solution. After heating (5 min at 1400 W and 20 min for cooling) 174 175 digests were diluted to 10 mL with ultrapure water for analysis by IC. Ion chromatograph was a 176 Metrohm 850 Professional IC (Switzerland) used under operation conditions listed in Table 1. Standard reference material NIST 1634c was used to validate the method with CI recoveries in 177 the range of 93 - 94%. 178

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180 2.2.4 *Electrometric analysis*.

181 Sample preparation followed steps prescribed by ASTM D3230 method [20]. Briefly, 10 182 mL of crude oil was diluted with xylene to volume of 50 mL. Mixture was shaken for 60 s and 183 further diluted to 100 mL with 63:37 1-butanol:MeOH with 3% water. Diluted samples were shaken 184 for 30 s and let to stand for 5 min prior to the measurement of their conductivity.

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187 3. Results and discussion

188 3.1 Modification of direct derivatization method

189 Previously published HS GC-MS/MS method was based on the direct reaction of Cl⁻ with

190 Et_3OBF_4 within the oil matrix according to equation 1:

191 Eq.1. $Cl^- + Et_3O^+ \rightarrow EtCl(g) + Et_2O$

The EtCl derivative was then detected by HS GC-MS/MS on a triple quadrupole platform and this approach was validated by analyzing NIST SRM 1634c fuel oil sample [14]. In this study, it was observed that for some types of crude oils the *in*-matrix derivatization was not a viable option due to insufficient resolution of EtCl from background interferences (Figure 1a). Furthermore, suppression of EtCl signal was also evident when the derivatization was carried out within the oil matrix.

Using the NIST17 MS libraries, the interferences eluting at 1.55 and 1.63 min (Figure 1b and 1c) were identified as 2-methylbutane (77% probability) and *n*-pentane (88% probability). Although hydrocarbon-based interferences could be resolved from EtCl by high resolution MS, such instruments are not widely available; therefore, to overcome this issue, an alternative approach which could eliminate alkane interferences at the sample preparation stage was explored.

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Figure 1. Determination of Cl⁻ in crude oil. (**a**) HS GC-MS SIM at m/z 64 chromatogram when Cl⁻ was derivatized directly within the oil matrix (light green line) and when derivatization was carried out after Cl⁻

water extraction (dark green line). (b) MS spectrum of the interference eluting at 1.55 min (identified as 1methylbutane). (c) MS spectrum of the interference eluting at 1.63 min (identified as *n*-pentane).

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The high solubility of CI^- in water allows its removal by phase extraction, as it was demonstrated in several published methods [7-10]. On the contrary, oil constituents such as 2methylbutane, *n*-pentane, or other alkanes are not water soluble. Therefore, water extraction of CI^- before derivatization would allow efficient segregation of matrix components interfering with the GC separation (Figure 1a) helping to improve the overall derivatization efficiency.

217 Water extraction is a small scale desalting process whose efficiency is sample-dependent: 218 complete extraction can be achieved in light crude oils, whereas heavy fractions may require repeated extractions [21]. Moreover, Cl⁻ can became trapped within stable emulsions which are 219 frequently observed with water treatment of heavy crude oils [1]. The proposed method 220 overcomes such matrix effects and issues of incomplete extraction/derivatization through the use 221 of species-specific ³⁷Cl⁻ enriched internal standard for isotope dilution guantitation [17]. When the 222 223 ³⁷Cl⁻ internal standard is added to the sample and reaches an equilibrium with the naturally 224 present Cl⁻ in the matrix, analyte losses due to incomplete extraction are compensated for. In isotope dilution quantitation, the isotope ratio $n({}^{35}CI^{-})/n({}^{37}CI^{-})$ is measured by MS which is largely 225 independent of matrix effects [22]. 226

Thus, prior to water extraction, crude oils were mixed with ³⁷Cl⁻ isotope internal standard and let to equilibrate. The equilibration of ³⁷Cl⁻ isotope with naturally present Cl⁻ isotopes was essential for obtaining valid quantitative results. The mixing conditions required to achieve complete equilibration between sample and internal standard were studied in two oil samples and the NIST SRM 1634c standard. A blend of sample and internal standard was prepared and analyzed by HS GC-MS at different time intervals. As shown in Table 2, the equilibrium was reached before/ or at least within 15 minutes of mixing.

Table 2. Effect of mixing time on isotope ratios (r_{AB}) and ratio precisions measured by HS GC-MS in samples S1, S4 and NIST 1634c spiked with ³⁷Cl⁻ r_{AB} (n = 3)

Time (min)	r _{AB} in S1	r _{AB} in S4	<i>r</i> _{АВ} in NIST 1634с
15	1.19 (1.1%)	1.36 (0.4%)	0.687 (0.5%)
30	1.19 (0.6%)	1.43 (0.1%)	0.685 (0.5%)
60	1.19 (0.4%)	1.42 (0.3%)	0.673 (0.1%)
120	1.17 (0.3%)	1.36 (0.4%)	0.666 (0.5%)

239 High Cl⁻ content and/or sample viscosity may require matrix dilution prior to analysis. Crude oils are complex mixtures where micro-droplets of water are dispersed in a non-polar 240 medium. The integrity of the sample may be altered if an improper dilution solvent is used. For 241 242 example, when crude oil was diluted with anhydrous toluene, a phase separation with solid 243 sedimentation was observed. In such instances, the homogeneity of the sample was compromised and, consequently, the reproducibility of Cl⁻ quantitation was poor. Asphaltenes in 244 crude oils form large aggregates and micelles [23] which can encapsulate nanoparticles and 245 246 micro-droplets of water. They are insoluble in normal paraffins such as *n*-heptane or *n*-pentane, 247 but they solubilise in aromatic solvents such as toluene, benzene, and xylenes [24]. Addition of 248 anhydrous toluene would improve the solubility of heavy fraction such as asphaltenes; however, 249 water addition is also required as explained in the next paragraph.

Reducing the water concentration in crude oil by dilution with anhydrous solvents may change the solubility of the matrix towards CI^- and cause its precipitation. A successful dilution of the crude oil is performed with a solvent that can efficiently solubilize both the hydrocarbon matrix and the salt component. In our previous study, it was demonstrated that CI^- solubility in organic solvents is dependent on the amount of dissolved water [14]. For example, an anhydrous *i*-PrOH:C₇H₈ 1:1 solvent mixture could not solubilize any CI^- , whereas upon addition of 5% water, up to 180 mg kg⁻¹ of Cl⁻ dissolved in the solvent blend (Figure 2). When the *i*-PrOH:C₇H₈ 1:1 solvent was spiked with more than 5% water, no increase of Cl⁻ solubility was observed and phase separation occurred above 7% water content. In this study, a blend of 1:1 *i*-PrOH:C₇H₈ with 5% water was selected for dilution of viscous samples and/or samples containing more than 20 mg kg⁻¹ Cl⁻. Care was taken to dilute the crude oils well below the solubility limit of 180 mg kg⁻¹ Cl⁻.

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Figure 2. Chloride mass fraction at saturation, $w(Cl^{-})_{sat}$, measured in the 1:1 *i*-PrOH:C₇H₈ solvent with increasing amounts of water.

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268 3.2 Validation of the novel approach

The extraction of CI^- to water phase has the advantage of greatly simplifying the matrix by reducing the presence of volatile organic compounds in the headspace. For this reason, EtCl acquisition was performed in SIM mode with a quadrupole MS detector. The water extraction step was necessary only when the sample contains C_5 hydrocarbons co-eluting with EtCl. Such interferences were not encountered in all crude samples. Light crude oils (API > 40) contain more volatile compounds which contributed to the observed interferences, while some heavy crude oils (see Table 4) could be analyzed using the *in*-matrix derivatization due to the absence of C_5 hydrocarbons [14].

To verify validity of the novel method, the HS GC-MS response of primary standards prepared either in water or in organic solvent (*i*-PrOH:C₇H₈ with 5% water) was tested. Six aqueous and non-aqueous Cl⁻ standards were prepared in the range 0.5 - 10 mg kg⁻¹ Cl⁻. Aliquot of 1 mL of each standard was spiked with ³⁷Cl⁻, derivatized with Et₃OBF₄, and analyzed by HS GC-MS. No statistical differences were observed between the instrument response of standards prepared in water or in organic solvent. This observation corroborated the ruggedness of isotope dilution in dealing with matrix effects.

Additional validation was performed by multiple measurements of NIST SRM 1634c where the novel method obtained a Cl⁻ recovery of 105% (RSD 3%, n = 9). This recovery compared favourably with *in*-matrix derivatization method, which was 107% (RSD 2%, n = 20) [14].

Although minor impurities of Cl⁻ were found in method blank, its signal was reproducible on day-to-day bases and average concentration of Cl⁻ in the blank was < 10 μ g kg⁻¹. A signal from 20 μ g kg⁻¹ calibration standard could be detected above the method blank and 100 μ g kg⁻¹ could be quantified with RSD < 13% (Figure 3). For crude oil samples that did not need solvent dilution prior to quantitation, we estimated a LOD of 30 μ g kg⁻¹ Cl⁻ and a LOQ of 100 μ g kg⁻¹ Cl⁻.



Figure 3. Overlaid GC-MS chromatograms of method blank with two aqueous Cl⁻ standards prepared at
20 µg kg⁻¹ Cl⁻ and 100 µg kg⁻¹ Cl⁻.

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297 3.3 Application of the HS GC-MS method within a collaborative study

298 To evaluate the performance of the novel method, a set of 21 crude oil samples was studied by four laboratories. Each participant used an in-house validated method for either total 299 300 Cl or inorganic Cl⁻ quantitation. To compare the performance with industry standardised method, a commercial laboratory performed quantitation using ASTM D3230 method for detection of salts 301 302 in crude oil, a proxy to estimate Cl⁻ contamination. Due to a limited amount of sample, only single measurement by ASTM D3230 could be performed and duplicate measurement was done on S12 303 304 to S21 heavy crude oils by CIC. All results are reported in Tables 3-4. Samples that did not contain 305 C_5 hydrocarbon interferences were analyzed with both *in*-matrix derivatization [14], and water 306 extraction. Particularly, four crude oils were analyzed by the two GC-MS approaches: S12, S19, 307 S20, and S21 (Table 4). Although Cl⁻ content in sample S19 was significantly higher when quantified by water extraction, it should be noted that for this sample w(Cl⁻) was close to LOQ. All 308 309 other three results were equivalent within the limit of the experimental error.

Table 3. Reported concentration (mg kg⁻¹ ± SD) in light and medium crude oils: inorganic chloride by HS GC-MS (n = 4) and ASTM D3230 (n = 1); total chlorine by CIC (n = 3), and microwave-induced combustion

Sample	GC-MS	CIC	MIC-IC	ASTM D3230
S1	8.48 ± 0.33	6.35 ± 0.01	NA	NA
S2	8.04 ± 0.38	6.35 ± 0.01	< 13	NA
S3	4.86 ± 0.15	8.22 ± 0.71	< 13	8
S4	69.9 ± 1.35	6.88 ± 0.10	62.4 ± 4.2	9
S5	4.46 ± 0.62	4.77 ± 0.18	< 13	5
S 6	5.96 ± 0.31	4.60 ± 0.71	< 13	8
S7	8.82 ± 0.16	10.2 ± 0.25	< 13	8
S 8	7.73 ± 0.09	10.3 ± 0.36	< 13	7
S9	5.36 ± 0.51	4.75 ± 0.64	< 13	7
S10	7.02 ± 0.08	11.6 ± 0.42	< 13	9
S11	6.34 ± 0.24	9.45 ± 0.43	< 13	8

313 ion chromatography MIC-IC (n = 3).

For light and medium crude oils, a general agreement between techniques was observed between reported results (Table 3). Observed deviations may be justified by sample inhomogeneity and/or unrepresentative sub-sampling. Additionally, HS GC-MS was designed to access directly Cl⁻, the CIC and MIC-IC measured total Cl, and the ASTM D3230 reported the Cl⁻ corresponding to the saline content of the sample as measured by direct conductivity. Organic Cl are rarely present as part of the geological formation, but can be incorporated during crude extraction, additives used during production, cleaning solvents used during operation or during

³¹⁴ NA – sample not available

³¹⁵

³¹⁶

transportation. If present, CIC or MIC-IC method would not be able to separate them from CI⁻.
Despite such fundamental differences in the definition of the measurand, the agreement between
the four independent methodologies was reasonable.

Apart from S4, the average difference between the various methods was within 2 mg kg⁻¹ Cl⁻ and, for the majority of samples, results agreed within 30%. Significantly higher concentration in S4 was reported by HS GC-MS and MIC-IC in comparison with CIC and ASTM D3230. Interestingly, when S4 was initially diluted in anhydrous toluene, the measured concentration of Cl⁻ was 27.7 mg kg⁻¹. The observed increase in measured concentration of Cl⁻ upon dilution in *i*-PrOH:C₇H₈ with 5% water indicates that some of the Cl⁻ present in the sample may be in particulate form with significant sample inhomogeneity.

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Table 4. Reported concentration (mg kg⁻¹ \pm SD) heavy crude oils: inorganic chloride by HS GC-MS/MS (*n* = 4), HS GC-MS (*n* = 4) and ASTM D3230 (*n* = 1); total chlorine by CIC (*n* = 2), and microwave-induced combustion ion chromatography MIC-IC (*n* = 3).

Sample	GC-MS/MS ¹	GC-MS ²	CIC	MIC-IC	ASTM D3230
S12	993 ± 103	866 ± 43.6	201.5 ± 9.0	538 ± 33	459
S13	-	94.4 ± 0.94	24.5 ± 1.0	85.7 ± 8.2	146
S14	-	3.14 ± 0.11	4.8 ± 0.1	< 13	15
S15	-	30.7 ± 0.52	24.5 ± 3.0	37.7 ± 2.6	44
S16	-	2.03 ± 0.11	3.25 ± 0.10	< 13	19
S17	-	268 ± 7.2	198	337 ± 26	330
S18	-	84.8 ± 2.57	93.5 ± 1.0	103 ± 9	114
S19	0.38 ± 0.02	0.62 ± 0.15	< 1	< 6.1	13

S20	8.71 ± 0.09	8.82 ± 0.09	9.45 ± 0.10	13.4 ± 1.2	36
S21	0.80 ± 0.14	0.89 ± 0.23	3.0 ± 1.0	< 6.1	23

¹ Direct derivatization HS GC-MS/MS [14]

² Water extraction followed by derivatization HS GC-MS (present study)

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343 As expectable, a much larger spread was observed within the results reported for the heavier crude oil samples (Table 4). Most challenging samples were those containing the highest 344 amount of Cl⁻ like S12, S13, and S17, having $w(Cl^-) > 100 \text{ mg kg}^{-1}$. Homogeneity issues related 345 346 to the limited CI⁻ solubility and possibly encapsulation of CI⁻ salts in crude oil matrix could have 347 contributed to the large disagreements in the reported results. For samples where $w(Cl^{-}) < 100$ mg kg⁻¹, we observed a preferential agreement between HS GC-MS and CIC method, whereas 348 349 the MIC-IC and ASTM D3230 gave higher estimates. In this regard, it is worth mentioning that the 350 ASTM D3230 may produce Cl⁻ overestimation when the sample matrix analyzed has a high water content, sediments, or other components that can contribute to the total reading of conductivity 351 [20]. However, we cannot exclude that the difference observed with the ASTM method are due to 352 artifacts induced by sample preparation. Such heavy crudes (in particular S19, S20 and S21) 353 were solid at room temperature, and S21 did not reach its pour point even upon heating at 60 °C 354 355 for 30 min. Therefore, the homogenisation of these samples could have impacted the accuracy 356 of the results.

In summary, the proposed HS GC-MS method was design for quantitation of Cl⁻ and showed good agreement with ClC, MIC-IC and ATSM D3230 methods, when analyzing Cl in medium and heavy crude oils. Furthermore, the use of ³⁷Cl⁻ internal standard played a major role in the control of matrix effects and contributed to robust quantitation by isotope dilution. Since the petroleum industry is concerned about inorganic chlorides, the specificity of HS GC-MS toward Cl⁻ is adding a high value to understanding the type of Cl present in crude oil. This information would be important for tuning the current technology used for crude oil salt removal. It should be noted that CIC and MIC-IC methods are set for total CI, thus, for a proper assessment, they need prior knowledge about the content of organochlorides. Similarly, ASTM D3230 assumes that matrix components other than CI have a negligible influence on the conductivity readings. This simplification may not be viable for all sample matrices, and overestimation of CI⁻ may be experienced.

369 When it comes to sample analysis, HS GC-MS required a low level of instrument maintenance: HS injections were essentially matrix free, thus the annual instrument maintenance 370 costs are significantly reduced. This in turn reduces the shut down time of the instrument, which 371 372 is often costly and allows the funds otherwise spent on instrument up keeping to be diverted towards growth and increased productivity. Another important benefit of HS GC-MS is the 373 significant increase of sample throughput achieved by short chromatographic run of 7 min. On 374 the contrary, CIC method requires 19 min run to elute all anion present in it the sample, MIC-IC 375 376 required additional steps for sample digestion, whereas ASTM D3230 method is based on manual data acquisition. 377

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4. Conclusion

380 The novel headspace GC-MS method enabled accurate Cl⁻ guantitation in a variety of crude oils with minimal sample preparation. Crude oils were diluted, mixed with ³⁷Cl⁻ internal 381 standard, water extracted, and derivatised with Et₃OBF₄ to convert Cl⁻ to volatile EtCl. Headspace 382 383 was analysed by GC-MS within 7 minutes allowing high sample throughput. Robust and accurate quantitation was obtained by isotope dilution. This high-precision quantitation approach could 384 correct for any analyte losses and matrix effects. The novel GC-MS method performed well in 385 comparison with industry standardised CIC, MIC-IC and ASTM D3230 methods for quantitation 386 of Cl⁻ in medium and heavy cut crude oils. As this method can be expanded to detection of other 387 388 halides in oil matrices, it may also provide a platform for multi-anion analysis. The availability of a

389	matri	x-insensitive method for specific detection of CI^- in crude oils will be of benefit to the	
390	petrochemical industry and could play a role for the standardization of reference procedures and		
391	certifi	ed reference material intended for the quality control of Cl⁻ in crude oils.	
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