



Development of a robust method for the determination of fluorine in liquid petroleum products

María Fernanda Gazulla^{*}, Marta Rodrigo, María Jesús Ventura, Cristina Andreu, Mónica Orduña

Instituto de Tecnología Cerámica, Asociación de Investigación de las Industrias Cerámicas, Universitat Jaume I. Castellón. Spain

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ABSTRACT

A robust method for the determination of total fluorine in liquid petroleum products is developed. The methodology is based on the oxidative pyrohydrolytic combustion of the sample, followed by the analysis of the evolved gases absorbed in an absorbing solution by ion chromatography. The detection limit reached for fluorine is $0.5 \text{ mg}\cdot\text{kg}^{-1}$ and the quantification limit is $1.4 \text{ mg}\cdot\text{kg}^{-1}$, thanks to the optimisation of different variables: combustion variables (temperature and time), sampling loop, and sample weight. The validation process has been developed by calculation of the uncertainty of the measurement and the analysis of spiked samples as there are no certified reference materials. The new methodology set up permits the determination of fluorine over organic materials from the refining industry of different matrices such as fuel oil, acid soluble oil, etc., containing from very low to high fluorine concentrations in a relatively short time, which makes the methodology suitable to be used as a control method. With this methodology, there is no need of sample preparation which implies the no use of acids for that, thus being environmentally friendly.

1. Introduction

Acid soluble oil (ASO) is formed as by-product in the isobutane alkylation with alkene in the presence of trifluoro methane sulfonic acid (TfOH). It is a complicated mixture of unsaturated hydrocarbons with conjugated double bonds, soluble in acids [1]. Due to its formation process, ASO presents fluorine in its composition.

The ASO is normally recycled but it can also be sold as residual fuel or burned in the unit's boiler. Although it is normally recycled, part of it can reach the production process and contaminate fuel with traces of fluorine [2].

Fluorine is high corrosive and poisons the catalysts, so its concentration must be thoroughly controlled to minimise the damages that might be caused in the refinery facilities.

Some literature roughly addresses fluorine analysis. Elvin and Ligett [3] mention a set of methods for the decomposition of fluorine organic compounds, including the oxidation method by oxygen combustion, although no quantitative results are shown. Fernandopulle and Macdonald [4] show results for the analysis of fluorine in organic compounds by spectrophotometric determination, obtaining good results in samples with a fluorine concentration higher than 15%, but not showing

the accuracy for samples with fluorine traces and presenting as main drawback the impossibility of analysing coloured samples, as fuels. Standard ASTM D7994 describes the methodology for fluorine determination by oxidative pyrolytic combustion followed by ion chromatography detection in liquid petroleum gas, low molecular weight hydrocarbons, their mixtures, and dimethyl ether (DME) in the range of $1 \text{ mg}\cdot\text{kg}^{-1}$ to $300 \text{ mg}\cdot\text{kg}^{-1}$, but it does not apply to heavy petroleum liquids as fuels [5].

No studies in the literature consulted for the determination of fluorine in the ASO or in fuels have been found, being these products the ones that must be thoroughly controlled to ensure the viability of a refining plant. Besides, given the peculiar process of ASO formation, it may result in the ASO showing variable fluorine concentration.

Goldschmidt et al. [6] focuses on the optimum conditions for chlorine extraction in heavy crude oils and measurement by ICP-OES in one of their publications but, although the operation conditions used could be similar to those for fluorine extraction, no comments about fluorine recovery are made. Druzian et al. [7] also published a study for chlorine extraction by pyrohydrolysis combustion and determination by ICP-OES, but fluorine was not analysed either.

The main objective of the present study is the development of a

^{*} Corresponding author at: Instituto de Tecnología Cerámica, Avda. Vicente Sos Baynat. s/n, 12006 Castellón de la Plana, Spain.

E-mail address: gazulla@itc.uji.es (M.F. Gazulla).

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robust and accurate methodology for the determination of fluorine in organic materials of different matrices in a wide range of concentrations, that can be used as a control method.

Wilson and Marczewski [8] published a study where samples of crude oils were submitted to a borax-alkali fusion followed by ion-selective electrode measurement. Although the authors did not observed loss of fluorine, high temperature needed for borax to melt makes it difficult to ensure total fluorine recovery. However, measurement of fluorine by ion-selective electrode is the reference method for the determination of fluorine in samples in aqueous medium. Considering these premises, first attempt was conducted submitting a sample of crude oil to an acid digestion by microwave using a single reaction sealed chamber digester model Ultrawave from Milestone to extract fluorine and measuring it by fluorine selective electrode. The solution obtained after digestion was so acid that had to be neutralized with a considerable amount of NaOH, presenting as a result high saline load which made the measurement by selective electrode impossible to carry out. Second attempt was based on the study carried out by Jones et al. [9] and the UOP Method 588 [10] for chloride determination in hydrocarbons, trying to extract fluorine with a combination of both methodologies, but fluorine recovery was very low. Final attempt was performed applying the extraction method for chloride in hydrocarbons with toluene to fluorine [11], but total recovery of the analyte was not reached.

Considering the unsuccessful attempts, the method was finally developed using oxidative pyrohydrolytic combustion, after optimising the heating treatment conditions, followed by ion chromatography detection. The methodology was optimised to get a robust method capable of analysing organic samples of different matrices, with low quantification limit and fast to be used as a control method.

2. Experimental

2.1. Instrumentation

The instrumentation used was a pyrolytic combustion unit connected to an ion chromatograph:

A) Pyrolytic Combustion Unit:

Combustion was performed using an automatic boat controller and an electric furnace model AQF-100, both from Mitsubishi Chemical Corporation. The furnace was provided with a combustion tube, made of quartz capable of withstanding temperatures up to 1100 °C. The system is also provided with a water supply unit model WS-100.

The formed gases were absorbed in a gas absorption module model GA-100 from Mitsubishi Chemical Corporation, having a 10-ml absorption tube which is filled automatically with a known volume of absorption solution by a built-in burette. The gas absorption unit is interfaced to an ion chromatograph (IC) and injects and aliquot of the absorption solution into the IC after the sample is combusted and the by-products of combustion absorbed.

Some operational conditions were fixed as follows:

- *Sample boat*: Quartz (As they are not porous, they avoid the absorption of the organic sample and, therefore, eliminate the memory effect)
- *Argon flow on AQF-100 (carrier)*: 200 ml·min⁻¹
- *Oxygen flow on AQF-100 (combustion agent)*: 400 ml·min⁻¹
- *Argon flow on WS-100 (humidification)*: 100 ml·min⁻¹
- *Water supply scale (on WS-100)*: 2
- *Absorption solution*: 30 ppm H₂O₂ and 0.5 ppm P
- *Absorption tube size*: 10
- *Absorption solution volume*: 5 ml

B) Ion Chromatograph:

Fluorine was analysed by an ion chromatography system model ICS-1000 from Dionex, provided with a guard column, an anion separator column, capable of producing satisfactory baseline separation of the fluorine anion peak, a cation suppressor column, and a conductivity detector.

2.2. Materials

The following organofluoride reagents were used for calibration and validation of the combustion ion chromatography procedure: 1H, 1H, 2H, 2H-perfluoro-1-decanol from Sigma-Aldrich and 4-fluorobenzoic acid (C₇H₅FO₂) from Aldrich.

Diethylene glycol diethyl ether from Sigma-Aldrich was used as diluent for calibration and validation standard preparation. The selection of the diluent was based on the capacity of dissolving the organofluoride reagents.

Different liquid petroleum products were selected for analysis: ASO, fluorine-exempt fuel (FO), fuel oil 1 (FO1), fuel oil 2 (FO2), and fuel oil 3 (FO3). Table 1 shows the API gravity of the samples selected for this study. The API gravity (American Petroleum Institute gravity) is a measure of how heavy or light a petroleum liquid is compared with water, thus being an inverse measurement of a petroleum liquid's density relative to that of water (also known as Specific Gravity (SG), an it is calculated from expressions (1) and (2) [12]:

$$SG = \frac{\rho_{\text{sample}}}{\rho_{\text{H}_2\text{O}}} \quad (1)$$

$$\text{API gravity} = \frac{141.5}{SG} - 131.5 \quad (2)$$

where ρ_{sample} is the density of the petroleum liquid product and $\rho_{\text{H}_2\text{O}}$ is the density of water, both measured at 15 °C (60°F), as it is stated in standard ASTM D 1250. The liquid petroleum classification according this parameter is shown in Table 2.

Sodium carbonate and sodium bicarbonate both from Merck were used for eluent solution preparation for IC measurement.

Hydrogen peroxide 30% from Panreac and 1000 mg·kg⁻¹ P from Merck were used for the preparation of the absorbing solution.

2.3. Experimental part

Oxidative pyrohydrolytic combustion is a process in which a sample is burned in an oxygen-rich environment at high temperature and in the presence of excess water vapor not originated from the combustion of the sample [5].

In this study, the optimisation of the extraction process for fluorine by Oxidative pyrohydrolytic combustion and the optimisation of its measurement by ionic chromatography was undertaken likewise other authors previously did for the analysis of chlorine in crude oils or in pharmaceutical excipients [6,7].

The setting up of the methodology consisted of the optimisation of the combustion and measurement step to reach exact and accurate results for all kind of samples. The studied variables were the following:

- Combustion tube temperatures: Inlet and Outlet
- Position and dwelling time of the boat inside the combustion tube

Table 1
Physical properties of the samples used to develop the method.

Sample	ρ_{sample} (kg·m ⁻³)	API gravity (°)	Classification
ASO	800	45.4	Light
FO	910	24.0	Medium
FO1	980	12.9	Heavy
FO2	940	19.0	Heavy
FO3	970	14.4	Heavy

Table 2
Liquid petroleum classification according to their API gravity.

	API gravity (°)
Light liquid petroleum	>30
Medium liquid petroleum	20–30
Heavy liquid petroleum	10–20
Extra-heavy liquid petroleum	<10

- Sample weight
- Sampling loop

Calibration and validation were carried out preparing standards from organofluoride reagents as there are no standard reference materials of liquid petroleum products with a certified fluorine value commercially available.

2.3.1. Optimisation of combustion conditions

First trials were undertaken setting the combustion temperature of the outlet tube at 1000 °C and the inlet one at a temperature of 900 °C. After that, both temperatures were decreased to 900 °C and 800 °C, as second trial, and 800 °C and 700 °C, in a third experiment, respectively to test if sample could be decomposed at a lower temperature which would mean a reduction in the energy consumption.

Once the furnace temperature was optimised, following experiments were conducted to decrease the quantification limit. The study was carried out increasing the sampling loop, so that the amount of sample introduced in the chromatograph be bigger and, therefore, the increasing the signal detected. Existing applications normally used sampling loops between 20 and 200 µL, while in this study, experiments with a sampling loop of 300 µL were performed to increase the minimum amount of fluorine that could be detected. Besides, although the experts in the instrument suggest that the maximum amount of sample that can be analysed is 500 mg (to ensure total combustion of the sample), sample weight was increased up to 700 mg to decrease the quantification limit either.

Last trials had the purpose of decreasing the total analysis time to be able to be used as a control method. For that dwelling times inside the combustion tube were modified, to decrease the combustion time as much as possible, and the results compared.

2.3.2. Measurement by ionic chromatography

Following the objective of developing a robust and exact method, measurement calibration and validation was not conducted with aqueous standards and direct calibration but with standards prepared in organic medium that were submitted to the same oxidative pyrohydrolytic combustion as the samples under study.

Calibration of the ion chromatograph was carried out preparing the calibration standards with an organofluoride reagent of known fluorine concentration diluted with diethylene glycol diethyl ether. Calibration standards were then submitted to the same oxidative pyrohydrolytic combustion as the samples. Following the same procedure, validation standards were prepared using different reagents from those used for calibration and submitting the sample to the same combustion process.

Different strategies were performed to determine the true value: on the one hand, samples of variable matrices with unknown fluorine concentration were analysed; on the other hand, and fluorine-exempt fuel oil was also spiked with known concentrations of fluorine for recovery calculation.

The recovery (R) was calculated using Eq. (3):

$$R = \frac{C_{obs}}{C_{RM}} \quad (3)$$

Where C_{obs} is the fluorine concentration of spiked sample when measured ($\text{mg}\cdot\text{kg}^{-1}$), and C_{RM} is the known concentration of fluorine of the spiked sample ($\text{mg}\cdot\text{kg}^{-1}$) [13].

Measurement uncertainty was calculated using the following expression:

$$U = k \cdot \frac{s}{\sqrt{n}} \quad (4)$$

where s is the standard deviation of the sample measurement under reproducibility conditions, and n is the number of measurements under reproducibility conditions. The coverage factor k is determined from the Student's t -distribution corresponding to the appropriate degrees of freedom and 95% confidence

2.4. Calculation of the detection limit (L_D) and quantification limit (L_Q)

The L_D was calculated from the measurement of a sample with a concentration 0.5 times the concentration of the lowest standard in the calibration curve for each analyte. The sample was measured ten times under reproducibility conditions. The detection limit was obtained in accordance with the International Union of Pure and Applied Chemistry (IUPAC) guidelines from the following expression:

$$L_D = 3.29 \cdot s \quad (5)$$

where:

s = value of the standard deviation of the measurements

The L_Q , which expresses the quantifiability of an analyte, was calculated according to the IUPAC guidelines as ten times the standard deviation of the measurement, for a number of measurements equal to ten [14,15]:

$$L_Q = 10 \cdot s \quad (6)$$

3. Results

3.1. Optimisation of combustion conditions

The optimisation of the combustion conditions was undertaken studying the following variables: the combustion temperature of the inner and outer furnace tubes, the sample weight used for analysis and the sampling loop size injected to the chromatograph, and the position and dwelling time of the crucible with the sample inside the furnace.

Combustion temperature

A validation standard of $10 \text{ mg}\cdot\text{kg}^{-1}$ F (in organic medium) was prepared to carry out the optimisation of the combustion conditions.

Table 3 shows the results obtained in the measurement of the validation standard of $10 \text{ mg}\cdot\text{kg}^{-1}$ F, together with their uncertainty, at the different combustion temperatures studied. The results shown are obtained as the mean of three different measurements undertaken in each condition tested. Calibration of the ion chromatograph was also done for each combustion conditions.

Two out of the three combustion conditions studied showed good results in the analysis of the validation standard, which were the ones that worked at temperatures of 1000 °C and 900 °C (outlet and inlet temperatures) and at temperatures of 900 °C and 800 °C (outlet and inlet temperatures). Working temperatures of 800 °C and 700 °C (outlet and inlet temperatures) led to wrong results. Consequently, combustion temperatures were set to 900 °C (outlet Temp) and 800 °C (inlet Temp) to reduce energy consumption, as there was not a higher recovery working at 1000 °C/900 °C. As samples under study are heavy, combustion is a difficult process that requires an appropriate control to avoid analyte losses and wrong results.

Sampling loop and sample weight

Sampling loop and sample weight were optimised to decrease the

Table 3

Results of the optimisation of the combustion temperature.

	Outlet temperature: 1000 °C Inlet Temperature: 900 °C	Outlet temperature: 900 °C Inlet Temperature: 800 °C	Outlet temperature: 800 °C Inlet Temperature: 700 °C
F (mg·kg ⁻¹)	9.7 ± 0.3	9.8 ± 0.3	7.9 ± 0.3

detection and quantification limits. Table 4 shows the results obtained in the analysis of synthetic standards with different fluorine concentration prepared from 4-fluorobenzoic acid ((C₇H₅FO₂) reagent and diethylene glycol diethyl ether, together with their uncertainty. Combustion conditions used were the ones previously optimised.

As shown in the results presented, the use of a higher sampling loop decreased the detection limit and a standard with 2 mg·kg⁻¹ could be quantified with guarantee, when 500 mg of sample are weighed. Besides, with the increase of sample weight, a standard with 1.5 mg·kg⁻¹ F, that was not detected in the chromatograph when 500 mg of sample were weighed, could also be quantified. However, 1 mg·kg⁻¹ F could not be detected even with the increase of sample weight and sampling loop. As a summary, 1.5 mg·kg⁻¹ F can be analysed with guarantee using a sample weight of 700 mg and a sampling loop of 300 µL. Sample weight and loop size variables are critical to reach the quantification limit required.

Position and dwelling time in the combustion cycle

Finally, the optimisation of the combustion step finished with the optimisation of the combustion cycle, trying to decrease the total analysis time to make the method faster. For that, different positions of the sample boat and dwelling time at a concrete position were studied. All the experiments carried out for combustion temperature, sampling loop and sample weight optimisation were undertaken using combustion Cycle 1 shown in Table 5. Many different experiments modifying the position of the crucible and the dwelling time were tested, most of them not giving good results for different reasons like not obtaining a total combustion of the sample or having a total or partial blockage of the absorption tube due to combustion residues that reached that point. After many trials, cycle 2 shown in Table 5 was the only, apart from cycle 1, with which good results were obtained.

Synthetic standards already prepared and analysed for the optimisation of the previous variables using Cycle 1, were then analysed (by triplicate) using Cycle 2, the results being compared in Table 6.

According to the results obtained, dwelling time could be reduced, and time expend for the combustion of the sample was reduced from 510 to 420 s. As a result, with the design method, the determination of fluorine can be undertaken in 25 min, which make it suitable to be used as a control method in refinery plants.

3.2. Calculation of the detection limit (L_D) and quantification limit (L_Q)

A detection limit of 0.5 mg·kg⁻¹ and a quantification limit of 1.4 mg·kg⁻¹ were obtained for the determination of fluorine in organic compounds by oxidative pyrohydrolytic combustion followed by ion chromatography detection, using the optimised conditions.

Table 4Results for the optimisation of sampling loop and sample weight using C₇H₅FO₂ for standard preparation.

F (mg·kg ⁻¹)	Sample weight(mg)	100 µL loop	300 µL loop
5	500	4.3 ± 0.5	4.9 ± 0.3
	700	5.3 ± 0.5	5.2 ± 0.3
2	500	Not Detected	1.9 ± 0.2
	700	1.3 ± 0.4	2.0 ± 0.2
1	500	–	Not Detected
	700	Not Detected	Not Detected
1.5	500	–	Not Detected
	700	Not Detected	1.6 ± 0.2

Table 5

Combustion cycles tested showing good results.

	Cycle 1		Cycle 2	
	Position (mm)	Dwelling time (s)	Position (mm)	Dwelling time (s)
Position and dwelling time inside the combustion tube	105	180	105	90
	150	30	150	60
	180	60	180	60
	End	150	End	120
	Cool	90	Cool	90

Table 6

Results for the optimisation of the combustion cycle.

	Cycle 1	Cycle 2
10 mg·kg ⁻¹ F	9.8 ± 0.3	9.7 ± 0.3
5 mg·kg ⁻¹ F	4.9 ± 0.3	5.2 ± 0.3
2 mg·kg ⁻¹ F	2.0 ± 0.2	2.1 ± 0.2
1.5 mg·kg ⁻¹ F	1.6 ± 0.2	1.5 ± 0.2

3.3. Analysis of unknown samples

Once the methodology was optimised, three samples of fuel oil of unknown fluorine concentration and presenting different viscosities were analysed. Table 7 shows the results obtained, together with their uncertainty.

Results showed good accuracy not only in low fluorine values (around 2 mg·kg⁻¹ F) but also for high values of fluorine (around 250 mg·kg⁻¹ F). Conventional methods present acceptable results for low fluorine contents but do not present a good reproducibility when the sample contains high concentration. Consequently, the developed methodology presents a wide working range.

In order to check the trueness of the results, a fluorine-exempt fuel oil was spiked with different quantities of the analyte. The sample was spiked with 1.5, 10, 100 and 1000 mg·kg⁻¹ of F with 4-fluorobenzoic acid and the recovery (R) was calculated from Eq. (3). Table 8 shows the results of the spiked samples and the recovery (R).

Good recovery was obtained in all the spiked samples analysed, the method being validated.

4. Conclusions

The methodology set up in this study allows for determining fluorine in organic samples of different matrices and origin. The method consists of a fluorine extraction process by oxidative pyrohydrolytic combustion and a measurement by ionic chromatography. Fluorine extraction is quantitative using the following operating conditions: an outlet furnace

Table 7

Measurements of samples of fuel oil of different characteristics.

	F (mg·kg ⁻¹)
FO1	4.2 ± 0.4
FO2	49 ± 9
FO3	2.2 ± 0.2
ASO	240 ± 20

Table 8Results and recovery obtained in the spiked samples analysed with C₇H₅FO₂.

Spiked samples	F (mg·kg ⁻¹)	Recovery (R) (%)
FO + 1.5 mg·kg ⁻¹	1.6 ± 0.2	107
FO + 10 mg·kg ⁻¹	9.8 ± 0.5	98
FO + 100 mg·kg ⁻¹	103 ± 11	103
FO + 1000 mg·kg ⁻¹	1010 ± 25	101

temperature of 900 °C and inlet furnace temperature of 800 °C, a sample weight of 700 mg, a sampling loop of 300 µL, and a combustion cycle 2 shown in Table 5 (with total combustion time of 7 min).

The method is robust and exact as the recovery results and uncertainties calculated show. Therefore, it can be considered as an appropriate method for the determination of fluorine in different liquid petroleum products from a refinery as acid soluble oils, fuel oils, etc.

The methodology is versatile enough to analyse fluorine from 1.5 mg·kg⁻¹ and it can be used as a control method because this versatility permits the analysis of any organic sample which fluorine concentration is between the range stated.

The developed methodology presents shorter analysis time and needs the use of fewer reagents compared with the ion selective electrode method. Besides, no sample preparation is needed so that the use of acids is not needed which makes the methodology more environmentally friendly.

CRediT authorship contribution statement

María Fernanda Gazulla: Conceptualization, Supervision, Project administration. **Marta Rodrigo:** Methodology, Investigation, Writing – review & editing. **María Jesús Ventura:** Investigation, Validation. **Cristina Andreu:** Investigation, Validation. **Mónica Orduña:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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