Extraction of Chloride of Bitumen Samples

The microwave-assisted solvent extraction method for the determination of the salt content in bitumen samples represents an efficient alternative to the rather time and cost consuming established methods (e.g. ASTM D6470, D-3230 or IP 77/72).

1 Introduction

Accurate salt content determination in petrochemical products such as crude oil and bitumen is of utmost importance to petrochemical companies. The presence of sodium chloride causes several problems during transportation and the following refining processes, such as corrosion in transportation lines, fouling, and deactivation of catalysts.
For these reasons refineries employ various desalination processes and analytical tests for the measurement of salt and water content present in crude oil and related petrochemical products.

Conventional and standardized tests for the determination of salt in crude oils and related petrochemical products are well established, but are known to be complicated and very labor intensive and time consuming.

Standard methods, for example, ASTM D-6470 and D-3230 as well as IP 77/72, are inefficient and are not applicable to a wide variety of petrochemical samples. ASTM D-6470 and IP 77/72 involve the extraction of water-soluble chlorides under atmospheric conditions combined with titration or potentiometric measurement.

Applying these methodologies to high-viscosity petrochemical products containing high amounts of water or solvent can lead to variable and erroneous chloride results.

The major limitations of the conventional tests can be summarized as follows:

- very high solvent consumption
- extraction temperature limited to boiling point of solvent mixture
- laborious setup of conventional glassware (round-bottom flasks, reflux condensers, etc.)
- limited applicability to petrochemical products with varying viscosities and water contents
- lack of reaction parameters documentation

This report describes the applicability of microwave-assisted solvent extraction by processing a variety of bitumen samples over several days, with subsequent chloride determination.

2 Instrumentation

The microwave-assisted extraction step was carried out with Multiwave PRO SOLV, the predecessor of Multiwave 5000, equipped with Rotor 8NXQ80 and Rotor 16HF100.

Using the same rotors and the Safety Module SOLV the methods are adaptable for Multiwave 5000.

Analysis of extracted aqueous phases for chloride content was performed with a Metrohm 761 Compact Ion Chromatography system.

Figure 1: Multiwave 5000

3 Experimental

3.1 Samples

Two diluted bitumen samples with varying matrix compositions were processed daily over a period of 10 days. These samples were supplied by a large multinational petrochemical manufacturer. The known chloride contents of the two bitumen samples were previously determined via a conventional extraction method based on IP 77/72.

Component	Content [%]
Bitumen	50 - 70
Naphtha	35 - 45
Xylene	1 - 3
Toluene	1 - 2
Water	0 - 3

Table 1: Average chemical compositions of diluted bitumen samples

3.2 Experimental Procedure

3.2.1 Conventional extraction technique based on IP 77/72

Approx. 40 g of the diluted bitumen sample were weighed into a 1 L Erlenmeyer flask. After addition of 120 mL of toluene and 100 mL of deionized water the reaction mixture was continuously refluxed for 2 hours.

A fraction from the cooled down aqueous layer was collected, filtered, and analyzed for chloride content.

3.2.2 Microwave-assisted extraction technique

Approx. 2-3 g of diluted bitumen sample was weighed directly into each NXQ80 vessel. After addition of 10 g of toluene and 12.2 g of deionized water a PTFE-coated stir bar was added to facilitate efficient phase mixture.

The vessels were closed, the rotor loaded and the following power program was carried out:

	Step	Power [W]	Time [min]	Fan	Stirring
1	Ramp	900	15:00	1	high
2	Hold	900	90:00	1	high
3	Cooling	0	15:00	3	off

Table 2: Power program used for Rotor NXQ80

Based on the measured maximum reaction parameters for NXQ80 (40 bar and 210 °C) we recommend the following temperature program as a starting point for transferring the method to Rotor 16HF100 equipped with p/T sensor:

	Step	Temp. [°C]*	Time [min]	Fan	Stirring
1	Ramp	240	30:00	1	high
2	Hold	240	80:00	1	high
3	Cooling	70	0:00	3	off

**p/T Sensor*

Table 3: Recommended temperature program for Rotor 16HF100

After cooling a fraction from the aqueous layer of each reaction vessel was collected for subsequent chloride analysis via ion chromatography.

4 Results

A comparison in terms of chloride concentration between microwave-assisted solvent extraction and conventional extraction is shown in table 4:

	Sample 1	Sample 2
IP 77/72 [mg/ml]	14.2	24.1
Mean, MW PRO SOLV (n=10) [mg/ml]	14.3	25.0
Min, MW PRO SOLV (n=10) [mg/ml]	12.7	22.9
Max, MW PRO SOLV (n=10) [mg/ml]	15.9	27.7
s, MW PRO SOLV (n=10) [mg/ml]	0.9	1.3
Mean recovery [%]	100.4	103.7

Table 4: Recovery for chloride using microwave-assisted extraction

The chloride concentrations obtained after both extraction methods fit to each other for both samples.

The microwave-assisted extraction also exhibits good repeatability, with all results being within 2 standard deviations of the mean result:
sample 1: 2s = 1.8 mg/L, 95 % confidence;
sample 2: 2s = 2.6 mg/L, 95 % confidence

5 Conclusion

Microwave-assisted solvent extraction is a viable alternative to conventional standardized methodologies for the extraction of salts from bitumen.

The major benefits that can be realized include:

- substantial reduction in organic solvent usage
- fast processing in closed vessels: extraction is not limited to the boiling point of solvent mixture
- high-throughput (up to 16 samples simultaneously)
- efficient stirring ensures an appropriate contact between sample and solvent and therefor allows the processing of a wide variety of petrochemical sample matrices
- full control and documentation of reaction parameters lead to high repeatability and reproducibility
- high safety standards

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