



The Investigation of precision of analytical methods for determination of salt content in Iranian crude oils

Ali Asghar Pasban^{a*} and Behrouz Nonahal^a

^a Research Institute of Petroleum Industry, Tehran, Iran

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ABSTRACT

In crude oil analysis, the determination of salt content is one of the most important parameters especially for refining and exporting industries. In this study, extraction followed by volumetric titration and electrometric procedure are performed for determining salt content for several Iranian crude oils. Also, the effects of disturbing agents such as increasing associated water for determining salt in crude oil were investigated for both methods. The results show when water content in crude oil is less than 0.05 weight percent, both methods are equally accurate for determining salt content, but when there is an increase in associated water content in crude oil, the electrometric method followed by volumetric titration method shows more accurate results in comparison with the extraction procedure.

1. Introduction

Existing salt content in crude oils can lead to serious problems during petroleum production, refining process, transportation, and also some related chemical and petroleum engineering processes. [1]. Sodium, magnesium, and calcium chlorides are almost always present in crude oils. Moreover, calcium cement and calcium carbonate should also be mentioned. The amount of mineral salts in crude oil depends on the formation pattern of crude oil and can reach up to 200000 ppm [2-3]. In addition,

the pollution of the crude oil transportation route may also be somewhat effective. The presence of salts in crude oil in addition to corrosion causes the following problems.

During the production of crude oil, due to the minor evaporation of the associated water happens in the effect of pressure drop between the bottom and the top of the well, causing the chloride to settle sodium is at the entrance to the well wall and the diameter of the well decreases.

To cater for such issues, fresh water well is injected to the well. In refineries, the existence of salt along with other factors such as wax and asphaltene causes the formation of deposits inside the exchanger tubes.

* Corresponding author email: pasbanaa@ripi.ir
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Consequently, the formation of deposits inside the exchanger tubes reduces the heat transfer; moreover, the formation of deposits (or sedimentation) in furnace tubes will produce coke [4].

Also, the presence of water and salt in some crudes and heavy crudes will cause an increase in the acidity number. In order to control and reduce the effect of water and salt on the acidity number, water washing process (dehydration) is employed prior to the desalter unit [5-7].

In order to control the corrosion caused by salt, its content should be less than 4 ppm or 2 pounds in 1000 bpd of the crude oil [8]. In crude oil sales contracts, salt content is one of the important parameters whose permissible amount is mentioned in the contract, and the seller is obliged to control it when producing and exporting. Therefore, in the laboratory of exporting terminals, the salt content is determined, and if it exceeds the permissible limit, the cargo will not be shipped to the oil tanker. Also, if the buyer finds a discrepancy in the amount of salt received, inform the seller should be informed. Moreover, if the buyer's claim is confirmed, the seller will be obligated to pay compensation on the basis of the contract. It should be noted that a salt content increase in crude oil exports could be detrimental to the reputation of the exporting company in the oil market.

With reference to the above, standard salt content determination during production, transportation, storage, and exportation to a petroleum company are important. Crude oil producing company has to control this parameter in equipped laboratories. Oil companies can monitor the amount of salt along with other key parameters such as API grade, water and sediment, hydrogen sulfide, and sulfur on a daily basis [10-11]. In addition to controlling the quality of production of its subsidiaries, they can well defend the interests of participating in necessary situations and avoid unnecessary losses as much as possible. The National Iranian Oil Company (NIOC) has also created a hardware infrastructure and the necessary software in this field, and its experts try to carry out the necessary research and update the present standards. They use the best internationally accepted

methods to control the quality of crude oil exports. For the time being, many of the production areas and exporting terminals use extraction and volumetric titration methods. Also, recently, it was stipulated or stated that volumetric titration method should be gradually replaced by the electrometric method.

The purpose of this research is to study the current methods of salt determination in petroleum laboratories and investigate comparative advantages and disadvantages of each method in conjunction with the project performed on "Salt content determination of Iran's crude oils at the Research Institute of Petroleum Industry in 2018".

2. Experimental Procedure

2.1. Material and Methods

In the laboratory investigation, crude oils with different characteristics for salt determination were selected to obtain a better comparison of the performance of standard methods at different conditions.

For this purpose, 6 samples of crude oils produced by National Iranian South Oil Company (NISOC) were selected. NISOC is regarded as one of the largest crude oil producers in the world and produces 85 percent of crude oil in Iran. The specifications of selected crudes are shown in Table 1.

In this study, for measurement of API grade of crude oils, a SVM equipment (model 2000) manufactured by Austrian company (Anton Paar) has been used to determine dynamic density and viscosity of the crude oils [12]. Also, for water and sediment tests, Hermle centrifuge (model ZK510) equipment manufactured by German company (Carlowitz) has been used along with ASTM D95 method [13].

For the determination of water content in crude oil, Carl Fisher (805 model titrando) test procedure has been adopted with the aid of ASTM D4377 [14]. For this purpose, a titration apparatus manufactured by Metrohm has been used. This apparatus uses a dual combination of platinum electrode to measure the amount of water in crude oil. The asphaltene is determined in weight percent using normal heptane and APD-500A automatic machinery manufactured by a Japanese Company called Cosmo which works

based on the ASTM D6560 which is equivalent to the standard IP 143 [15].

Also, a titration apparatus manufactured by Metrohm (805 Titrando model) is used to determine the estimate the effect of salt on the acidity number of the selected crudes. Moreover, the titration apparatus manufactured by Metrohm is equipped with a combination of a silver glass electrode and silver chloride (Ag/AgCl) as reference electrode surrounded by the same electrode [16].

The acidity number is the amount of consumed hydroxides for neutralization of one gram of sample mgKOH/gram oil. The results obtained in this study showed that the crude oils used in this study had low acidity numbers and did not cause much disorder in the performance of desalting units [17].

2.2. Salt content determination by standard method IP 77

In this method, salt content in the crude oil is separated by a glass system manufactured by Petrotest which is designed based on the standard IP 77 [14]. In this extraction method, the sample is heated by an electric heater in a glass flask with the volume of 55 cm³. About 155 ml of crude oil with 155 ml of distilled water are poured inside the flask. After mixing, 100 milligrams of toluene and then 20 ml of acetone were added to the mixture. The flask is heated by the electric heater to the boiling point of the mixture, and the resulting vapors are cooled and returned to the flask by a vertical condenser mounted on top of the flask. This operation lasts for at least 45 minutes. To make sure that full salt extraction can be performed at a greater time. After completion of the extraction stage, the contents of the cooled water phases and organics are separated

and discharged through the valve embedded under the flask, and then the water phase is separated, and chlorine ion content in the water phase is neutralized by a mohair volumetric titration method. In this way, by using normal 0.01 silver nitrate, chloride ions are titrated in the presence of a few drops of potassium dichromate solution with a concentration of 50 gram. At the end of the neutralization of chlorine ions, the ambient color changes from yellow to light red. In this way, the concentration of chlorine ion is obtained in milligrams per cubic meter from Equation 1.

$$X = [VA/(V1-VB/V2)].N.58500.VE/VS \quad (1)$$

where, VA is the volume of silver nitrate solution used for the titration extraction in ml, VB is the volume of silver nitrate used as the titration witness, V1 is the volume of consumed extraction used in titration, V2 is the volume used as witness in the titration process, VE is the total volume of the extract, VS is the sample volume of crude oil used, and N is the normality of the silver nitrate solution.

2.3. Salt content determination by ASTM method D3230

To determine salt content by the above method, a digital analyzer (694-SICT Model) is used which is manufactured by Kohler Corporation. This apparatus measures the electrical current passing through the crude oil solved in a beaker of solution mixture of alcohols with the aid of an electrode based on the electrometric measurement method [17]. With respect to standard calibration curve of the apparatus, the passing flow is reported in terms of Micro Siemens to milligrams which is directly converted to cubic meter and displayed on the monitor. The electrode used consists of two platinum

Table 1. The specification of crude oils.

| Crude oil No. | API | Water Vol.% | Water and Sediments Vol.% | Acidity No. mgKOH/gr | Asphaltene wt.% |
|---------------|------|-------------|---------------------------|----------------------|-----------------|
| 1 | 33.3 | 0.025 | 0.05 | 0.05 | 1.0 |
| 2 | 33.2 | 0.025 | 0.10 | 0.08 | 1.1 |
| 3 | 30.4 | 0.20 | 0.30 | 0.15 | 1.9 |
| 4 | 31.3 | 0.75 | 1.0 | 0.17 | 2.0 |
| 5 | 24.3 | 1.0 | 1.0 | 0.31 | 4.7 |
| 6 | 18.5 | 2.0 | 2.0 | 0.40 | 8.4 |

plates with the dimensions of 25 mm × 50 mm which are placed in parallel facing each other.

The spacing between the plates is 2 mm, and the maintaining material which holds the plates next to each other is insulated. For calibration of the system, according to ASTM D3230, standardization of apparatus solution has been carried out through a mixture of alcohols that were diluted in a mixture of sodium, magnesium, and calcium solution chlorides of 70%, 20% and 10% respectively. The purpose of dilution is to prepare salts mixtures with a concentration of 0.1 g/m³. The mixture of alcohols contains 37 % vol. of pure ethanol in isobutanol, for any liter of which, 3ml of distilled water is added. At this stage, a quantity of about 10 ml of an oil cut like paraffin was thoroughly dissolved in 40 ml of an organic solvent such as Xylene. Then 50 ml of alcohol mixture was added to this mixture and severely stirred. Then the final solution was poured inside a clean beaker and its conductivity was measured. This result is in fact, the amount of conductivity of the control solution. Then to completely cover measuring range of the apparatus (0-430 mg/cm³), standard solutions were used to match the table presented in ASTM standard D-3230 containing 50 ml of solution of mixture of alcohols with a suitable amount of salt mixtures. During each step, the conductivity was recorded on the apparatus. In this way, there are about 10 points to plot the calibration curve.

After calibration of the apparatus, salt content of crude samples were determined. To do this, 10 ml of each crude oil sample was dissolved in an organic solution containing xylene and 50^{cc} of alcohol mixtures. At this stage, the mixture was stirred for 90 seconds by hand. Then the sample remains constant for 5 minutes. Finally, the content was poured in the special beaker, and the salt content was measured.

3. results and discussion

Salt content of samples of crude oils were measured using extraction and volumetric method (IP 77). In addition, the electrical conductivity measurement method (ASTM D3230) reported in Table 1.

The results of salt determinations are reported in Table 2. As it can be seen from Table 2, at low salt concentrations in crude oils, the values obtained are close to each other by both methods, but at higher concentrations, the measured values in the electrical conductivity method are very different from extraction method and in the case of crude oil, the difference is approximately 1.5 times more than the amount of extraction method due to the restriction in neutralizing process IP 77 method because in volumetric titration, the 0.01 solution of normal silver nitrate is used. Silver nitrate reacts only with the chlorine ions of the water-soluble salts derived from the extraction, and since the amount of silver nitrate which has been consumed is the calculation criteria for the determination of salt, the presence of the other forms of salts in the aqueous phase cannot be reported in this method.

As stated in this standard, only the amount of chloride ion should be reported in the final report. Therefore, it is suggested that in laboratories, which crude oil quality control is performed, should not report the final result as salt content when working with this standard. In this study, for further analysis of the reasons for the difference in the results, associated water of 6 samples of crude oils related to desalting units were analyzed for the above-mentioned methods. Table 3 shows the analysis of the results of 6 samples of associated water with crude oils. For determination of ions in water of crude oils, despite high chlorine ions, the other ions are not negligible. By increasing associated water, the error of measurement of ions using the conductivity method was increased (Table 3). In addition, this difference is shown in figure 1. As shown in this figure, the results of the salt obtained through the electrometric method are higher than the extraction and volumetric method, which indicates that this method is more precise. As shown in Table 3 with increasing associated water in crude oil, the amount of salt will also increase proportionally. On the other hand, as shown in Table 3, sulphate, and bicarbonate foundations can also be problematic for refineries, and therefore, the salt determination for crude oil

Table 2. The results of salt determination in crude oils.

| Crude Sample No. | Salt (mg dm ⁻³) | |
|------------------|----------------------------------------------|------------|
| | Chlorine Ion (mg dm ⁻³) IP 77 | ASTM D3230 |
| 1 | 33±2 | 34±1 |
| 2 | 65±1 | 72±3 |
| 3 | 146±5 | 160±2 |
| 4 | 194±7 | 295±5 |
| 5 | 203±6 | 344±4 |
| 6 | 207±12 | 395±9 |

should be calculated and total salt amounts should be reported for desalting units, so, the technical section will be able to control the output salt content by optimizing of parameters in desalting unit.

4. Conclusions

In this study, the determination of salt content in crude oils was evaluated by two methods which was exported and transported to domestic Iranian refiners. This procedure, was carried out on six petroleum products, produced by NISOC (National Iranian Southern Oil Company) using extraction and volumetric methods by (IP 77) and ASTM method D 3230. The results show that the electrometric method has some advantages in comparison to the extraction method, outlined as follows:

- With respect to the need for refiners the salt content of the crude oil as feed should be reduced to less than 3 ppm. For such scenarios, only the ASTM method D 3230 should be used because the lowest limit of measurement for the IP 77 method is about 20 ppm.
- Due to the nature of the IP 77 method, only chlorine ions in crude oil can be measured and, in the case of presence of salts in the form of sulfates or bicarbonates in the crude oil, these compounds cannot be calculated. Therefore, the total salt content

of crude oil cannot be determined by this method.

c) In the electrometric method, a smaller sample volume is needed compared to the time-consuming extraction method.

d) Repeatability and reproducibility of the results in the electrometric method are better than the extraction method and volumetric analysis.

e) It is recommended that the electrometric method for determining salt content be used when the amount of water in the crude oil is high. Therefore, in this method, the passing flow through the medium is used. Moreover, in this method, the concentration of total ions can be calculated, and thus a more accurate calculation of the inorganic salts can be achieved. This method also helps the utilization of optimized operation of existing oil installations against damages inflicted from corrosion and sediments.

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6. References

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Table 3. Ion compounds in water with crude oil number of chlorine ion.

| Sample No. | Chlorine Ion g L-1 | Sulphate Ion g L-1 | Bicarbonate Ion g L-1 | Specific Gravity |
|------------|-----------------------|-----------------------|--------------------------|------------------|
| 1 | 81 | 0.41 | 0.27 | 0.9882 |
| 2 | 79 | 0.35 | 0.27 | 1.0006 |
| 3 | 85 | 0.34 | 0.27 | 1.0961 |
| 4 | 87 | 0.32 | 0.33 | 1.0983 |
| 5 | 91 | 0.47 | 0.28 | 1.1024 |
| 6 | 105 | 1.42 | 0.30 | 1.1196 |

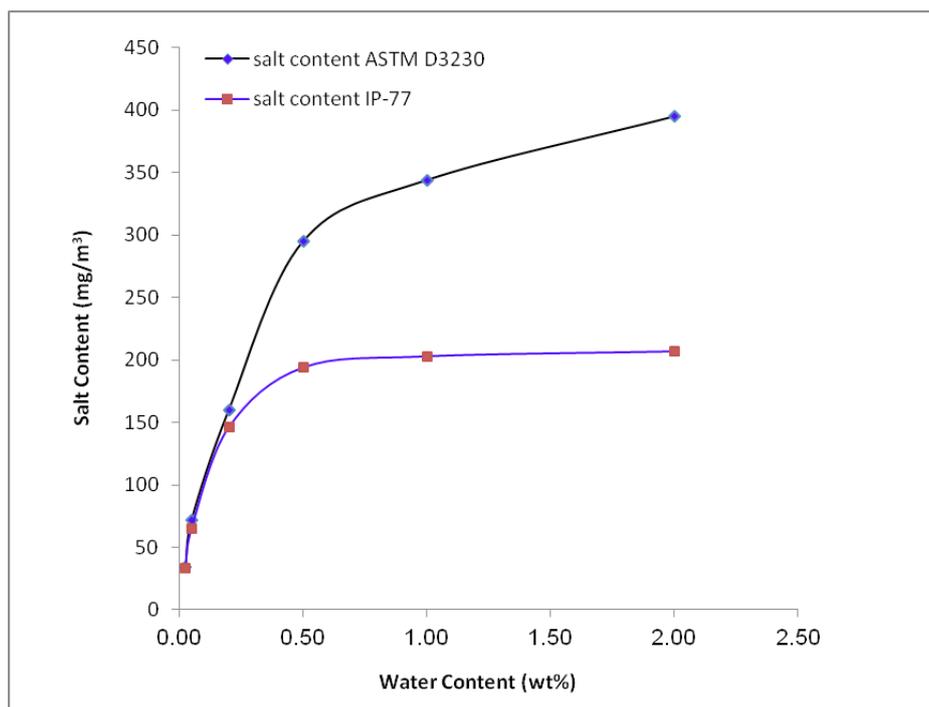


Fig. 1. Effect of increasing associated water in salt content determination.

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