RICE UNIVERSITY

Manual 1

Non-aqueous Phase Titration for Total Acid Number of Crude Oil

Yu Bian
08/10/2009

Prepared by Yu Bian, August, 2009

Name	Comment	Date

Contents

1. Non-aqueous Phase Titration

Acid number is defined as the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to specified end point. Here, spiking method[1] is used, because ASTM (American Society for Testing and Materials) standard procedure[2] requires large amount of sample, 20 g oil sample if acid number is less than 1 mgKOH/gOil. In addition, the titration inflection point by ASTM is frequently ambiguous. However, measurement of acid numbers measured by spiking method not only requires smaller sample, 0.5 to 2.0 g oil, but also yields a clear inflection point. This manual is prepared for measuring acid number of the crude oil samples, including detailed discussion.

1.1 Materials

1.1.1 Solutions

(a) Organic Solvent (1000ml)

50% toluene (HPLC grade), 49.5% 2-propanol (HPLC grade) and 0.5% deionized (DI) water (18.2 MΩ) in volume ratio. This solution is used for most oil samples, but it is changed in some special case, please see exception in 1.4.6.

(b) Spiking Solution (250ml)

Stearic acid dissolved in the organic solvent at a concentration of 0.02 M.

(c) Blank

75 ml organic solvent with 1 ml spiking solution. More organic solvent is needed when using larger sample or some special case, as shown in 1.4.6.

(d) Titrant (500ml)

1.0 M tetrabutylamonium hydroxide (TBAOH) in methanol is bought from Sigma-Aldrich and is diluted by ethanol to 0.05 M.

(e) Calibration solution (1000ml)

0.002 M potassium hydrogen phthalate (KHP) in DI water

1.1.2 Oil Sample

Crude oil is centrifuged before the titration to remove the water.

0.5-2 g crude oil is dissolved in 75 ml organic solvent with 1ml spiking solution. Use larger sample size when acid number is small as discussed in 1.4.4 and 1.4.6.

1.2 Equipment

Titrator: 716 DMS Titrator connected to a computer is used for automatic titration and data collection.

Metrohm Solvotrode: a glass electrode (6.0229.100) is used in organic solvent. It is a combination electrode and its reference electrolyte solution is 0.4 M Tetra Ethyl Ammonium Bromide (TEABr) in ethylene glycol. If not specified, the samples were titrated by this electrode. This electrode was compared with Metrohm General and Orion 8165 in 1.4.1.

1.3 Procedure

1.3.1 Conditioning the Electrode[3]

Preparing the electrode for a titration after long storage

- Immerse the pH-sensitive glass membrane (but not the ground-joint diaphragm) in distilled water for one minute to hydrate it.
- Open the refill aperture for the reference electrolyte by sliding down the rubber ring covering it.
- Slightly lift the ring-shaped sleeve of the ground-joint diaphragm and allow a little electrolyte to flow out. Carefully slide the sleeve back into its original position without exerting too much pressure. If the ground-joint sleeve seize up, immerse it in hot water for about one minute before you again carefully try to loosen the sleeve.
- Rinse the electrode with distilled water without letting any water enter its interior.
- Fill the reference electrode with its electrolyte solution up to the refill aperture and close the refill aperture.
- Soak the electrode in DI water overnight before use if the electrode was previously originally stored in its electrolyte solution. See in 1.4.2.
- Open the refill aperture.
- Measure the potential difference (mV) between two buffer solution, pH=4 and pH=7, and the difference should be at least 150 mV at 25 ℃.
- Precondition the electrode in organic solvent for 30 min before the first titration. See in 1.4.2.

Preparing the electrode for a titration daily

- The pH-sensitive glass membrane of the electrode should be immersed in distilled water overnight. (but not the ground-joint diaphragm)
- Open the refill aperture for the reference electrolyte by sliding down the rubber ring covering it.
- Fill the reference electrode with its electrolyte solution up to the refill aperture.

- Precondition the electrode in organic solvent for 30 min before the first titration. See in 1.4.2.

Between titrations

- Keep the refill aperture during titration.
- Rinse the electrode with the organic solvent.
- Rinse the electrode with DI water.
- Check whether the ground-joint diaphragm is blocked, i.e. whether you can see any deposits in the ground joint. If it is blocked, repeat the steps mentioned above for preparing the electrode.
- Rinse the electrode with the organic solvent.
- Precondition the electrode in the organic solvent for 3min between two titrations. See in 1.4.2.

Cleaning after the end of the titration

- Loosen the ring-shaped sleeve of the ground-joint diaphragm of the electrode.
- Remove any contamination of electrode caused by the sample with a suitable solvent, e.g. toluene.
- Rinse the electrode with distilled water
- Fill the reference electrode up to the refill aperture.

Storing the electrode

Storage periods of several days:

- Close the electrolyte refill aperture.
- Store the electrode in the corresponding reference electrolyte.

Shorter storage periods:

- Close the electrolyte refill aperture.
- Immerse the pH-sensitive glass membrane (but not the ground joint diaphragm) in DI water.

1.3.2 Titration Parameters

Titrant is delivered with the volume steps of 0.02 ml. Dosage rate is ≤0.2 ml/min. (TAN or stearic method in the computer). See discussion part in 1.4.4.

1.3.3 Titrant Calibration

Titrant concentration is calibrated by KHP aqueous solution. The concentration of TBAOH is calculated by $C_{KHP}xV_{KHP}/V_{TBAOH}$. Usually, the concentration of KHP is 0.002M. 50 ml KHP is titrated by TBAOH to get the inflection point to calculate the concentration of TBAOH.

1.3.4 Controlled Experiment[4]

Spiking solution (1.1.1(b)) will be used here as standard. The measured concentration should agree with the prepared concentration. Various volumes of spiking solution are diluted by same amount of organic solvent. The volume of titrant is plotted versus the volume of spiking solution and then the slope can be calculated as shown in Figure 1-1. Measured concentration of stearic acid in spiking solution can be calculated from this slope.

$$C(stearic) = slope \times C(TBAOH) \quad (1\text{-}1)$$

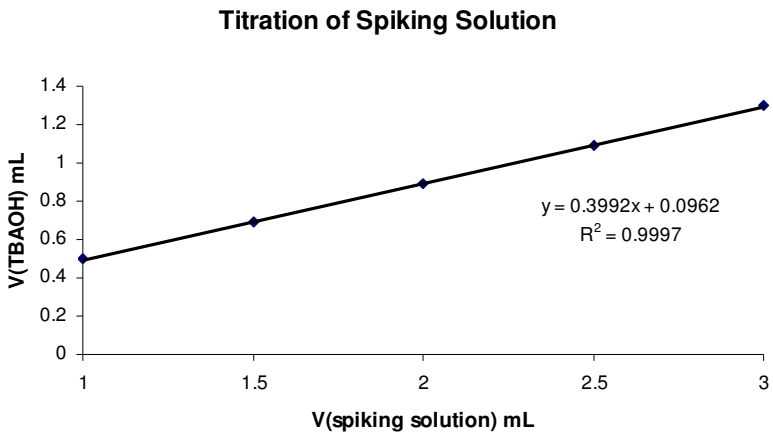

Figure 1-1. Volume of titrant versus volume of spiking solution (75 ml organic solvent)

Because the line intercept is not zero, Figure 1-1 indicates that the titration is sensitive to the amount of organic solvent. Thus, it is important to keep the volume of organic solvent same for sample and its blank.

1.3.5 Titration of Oil Sample

Titrate blank solution and oil sample (1.1.2). Each oil sample titration should have one parallel blank titration with same amount of organic solvent (reason is shown in 1.4.5). The titration results of Marathon Yates sample labeled as MY8 and its blank solution are shown in Figure 1-2.

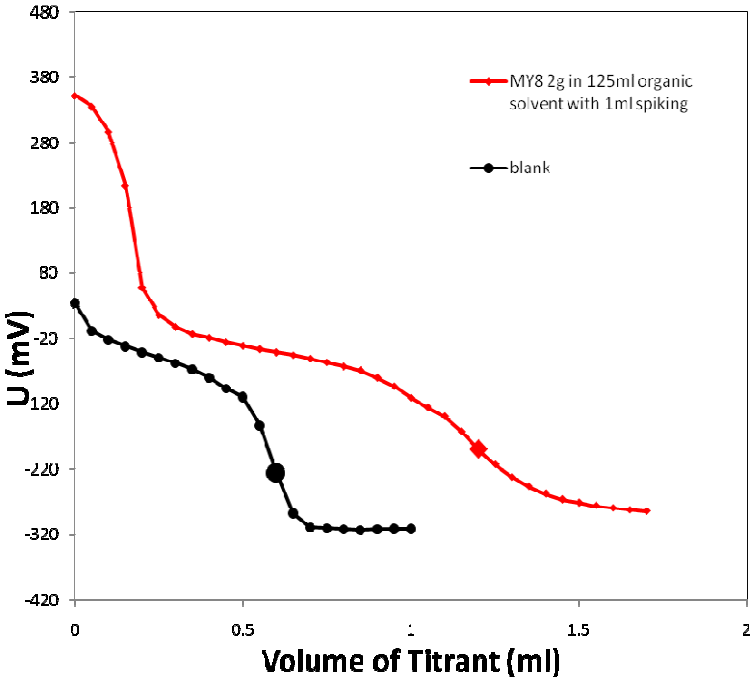

Figure 1-2. Titration of Yates MY8 and its parallel blank and the big symbols shows the inflection point

Acid number can be calculated by

$$AN = (V_i - V_b) \times C_{TBAOH} \times Mw / W_{oil} \quad (1\text{-}2)$$

Where, *AN*: acid number (mgKOH/gOil); V_i: volume of titrant at the oil sample inflection point (ml); V_b: volume of titrant at the blank inflection point (ml); C_{TBAOH}: molar concentration of TBAOH (M); *Mw*: molecular weight of KOH (56.1g/mol); W_{oil}: weight of the oil sample (g).

When the titration curve is not smooth and gives multiple end points, the end point can be obtained by the cubic equation fitting and the details will be shown in a separated chapter.

1.4 Discussion

1.4.1 Electrode[4]

Three electrodes were compared. Their properties were listed in the table below.

Table 1-1 Properties of different electrodes

	Metrohm Solvotrode	Metrohm general	Orion 8165
Electrolyte Solution	0.4 mol/L Tetra Ethyl Ammonium Bromide	3 mol/L KCl in DI	3 mol/L KCl in DI
Diaphragm	Ground-joint	Ceramic plate	Epoxy body

Metrohm Solvotrode was chosen over the other two electrodes because it has faster and more stable response in organic solvent. For this particular electrode, the filling solution TEABr in ethylene glycol is soluble in the organic solvent. In contrast, Orion and Metrohm general electrodes use nearly saturated KCl as the filling solution. This leads to the build-up of KCl precipitate on the diaphragm, which impedes the ion transport (see Figure 1-3). Furthermore, Solvotrode's ground-joint allows inner electrolyte solution to flow out of the aperture covered by the porous glass, which makes it easy to clean. However, the diaphragm in Metrohm general is made of a ceramic plate. When contacted with crude oil, the solid

contaminants in oil may clog the pores in the ceramic plate and damage the electrode.

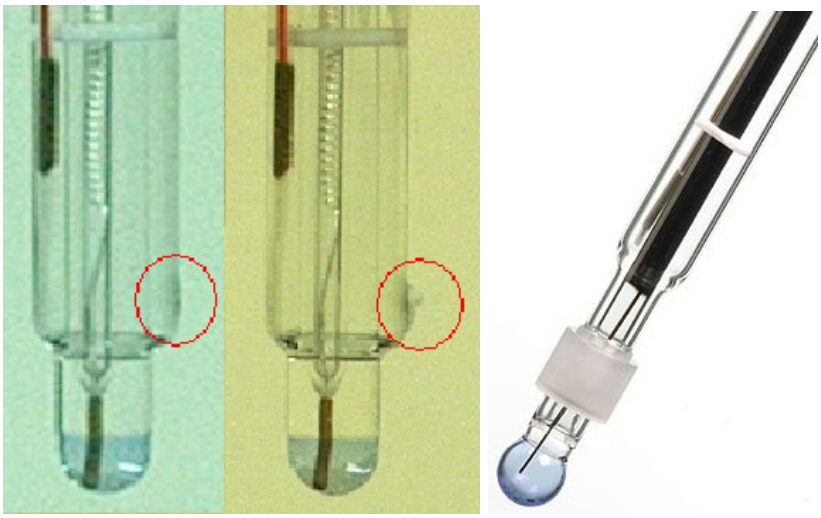

Figure 1-3. Metrohm general and Metrohm Solvotrode electrode. Left: Metrohm general: before contact with organic solvent diaphragm is clean of precipitates; middle: Metrohm general: after contact with organic solvent KCl precipitates around diaphragm; right: Metrohm Solvotrode electrode

1.4.2 Precondition[4]

In order to keep the potential of a glass electrode constant, the ion exchange across the membrane must have reached a stable condition. Conditioning electrode in suitable electrolyte is necessary to ensure an initial solvated layer condition that is as stationary as possible so that the results can be as reproducible as possible. The electrode should be preconditioned in the titration solvent as described in 1.3.1, as well as between two successive titrations to restore its response. Preconditioning is important in both non-aqueous and aqueous titration as shown below.

Precondition in organic solvent for non-aqueous titration

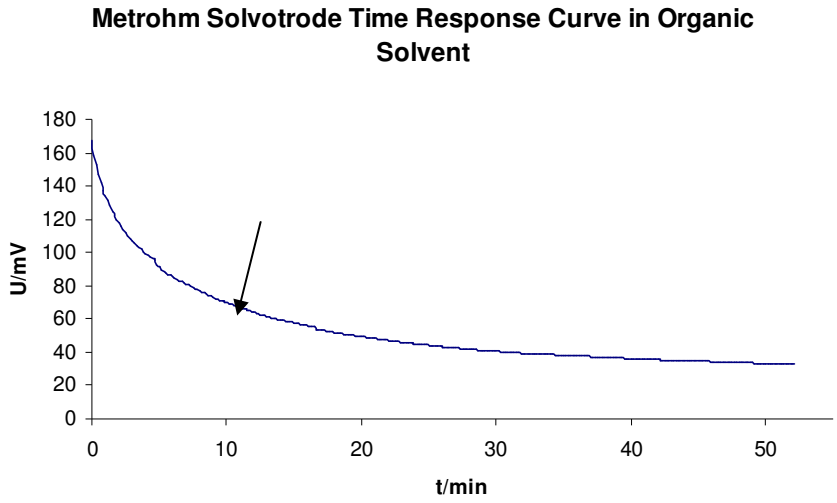

Figure 1-4. Metrohm Solvotrode responses in the organic solvent. Initial condition: electrode had been soaked in DI water overnight

The curve in Figure 1-4 is used to determine how long the electrode should be preconditioned. If we want the change in EMF to be less than 5% between two additions of titrant, the rate of change in EMF should be less than $5\%\Delta U / \Delta t$. Here, ΔU is the minimum difference in EMF between two additions of titrant and is about 5 mV from most experiments; Δt is the time interval between two additions of titrant and is about 10 sec. So the rate of EMF change is 1.5 mV/min. This can be satisfied by 14 minutes of preconditioning as shown by the arrow in the above plot. In real cases, however, preconditioning time was set as 30 minutes.

Titration results with and without preconditioning of the electrode in water are compared in Figure.1-5.

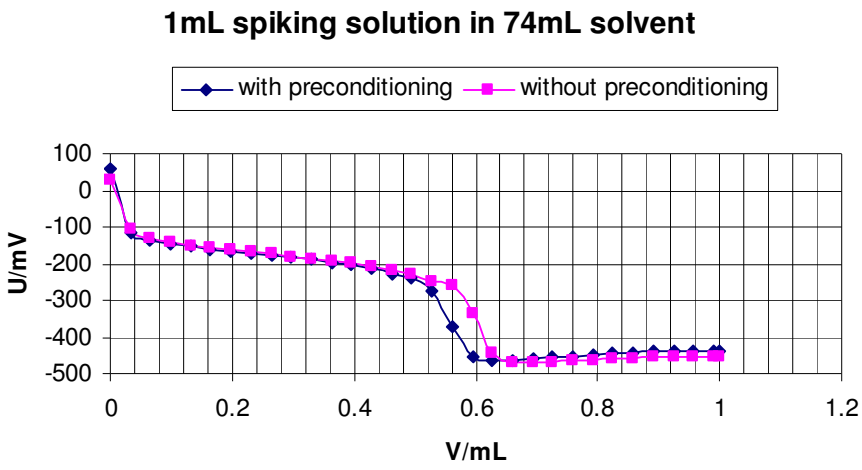

Figure 1-5. Two blank titrations with and without preconditioning. Inflection points V(red)=0.596 mL, V(blue)=0.559 mL. Relative error=6.6%

Precondition in DI water for aqueous titration

TBAOH (0.0500 mol/L) was calibrated by delivering TBAOH to 75 mL 0.00200 mol/L KHP aqueous solutions. Figure 1-6 shows that titration without preconditioning on day 1 gives C_{TBAOH}=0.0440mol/L. However, titrations with precondition in DI water for 5 minutes on day 1 and overnight on day 2 give C_{TBAOH} =0.0500 mol/L, which is in accordance with the prepared concentration. The electrode response in DI water as shown by Figure 1-7 indicates that Metrohm Solvotrode restored quickly.

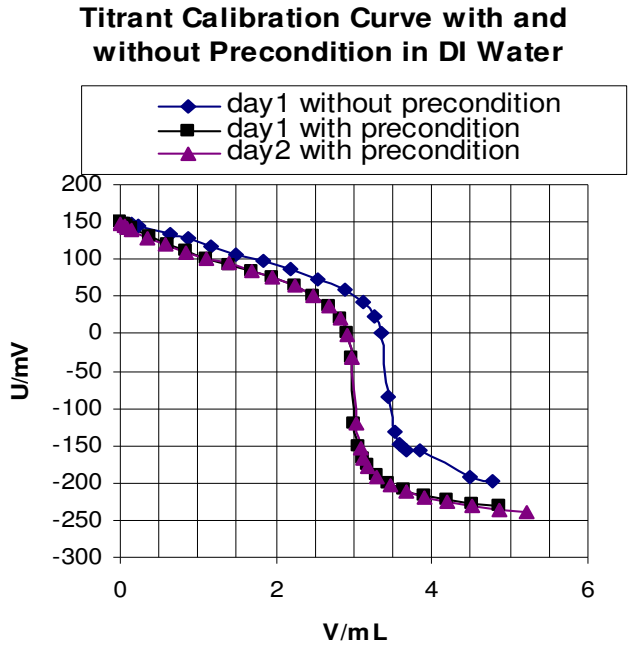

Figure 1-6. Titrant calibration curve with and without Precondition

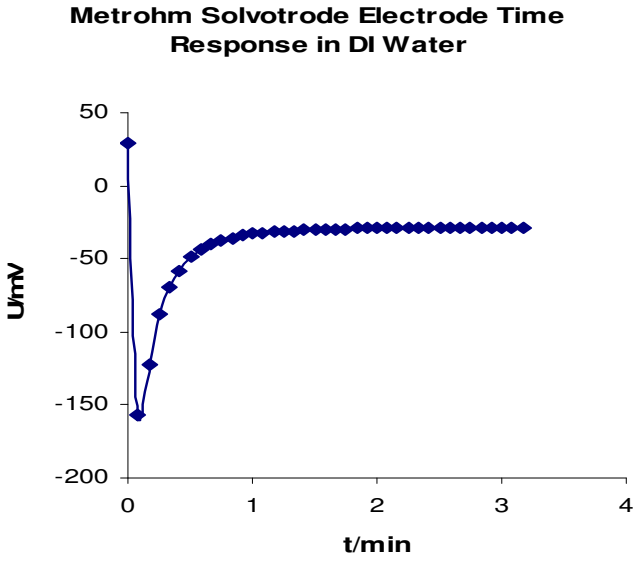

Figure 1-7. The electrode responses in DI water. Initial condition: electrode was soaked in the electrolyte solution (TEABr in ethyleneglycol)

1.4.3 Electrode response with contact of crude oil or blank solution[4]

It was reported by New Mexico Tech that whether blank titration was performed before or after oil titration made a dramatic difference [Fan and Buckley, 2008]. Blank titration before oil titration would give $V_b > V_i$, which would result in a negative acid number value. However, if the blank was measured after oil titration, they had $V_b < V_i$. According to them, only if the blank was measured after contact with the crude oil (the electrode response was affected for both measurements in the same manner) could a realistic measure of acid number be obtained. This phenomenon of dramatic change in blank titration curve was not observed in either MY6 or Q-Sand titration result as shown in Figure 1-8 and 1-9.

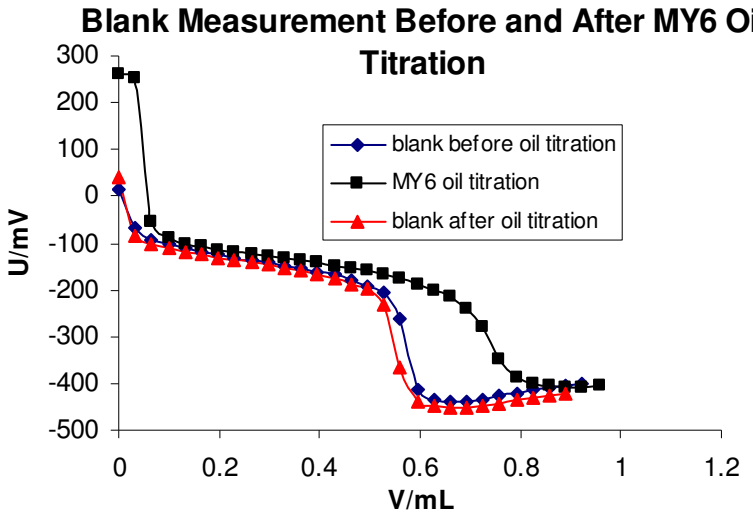

Figure 1-8. Blank measurements before and after MY6 oil titration. Exposure to MY6 crude oil sample does not drastically change the electrode response. V_b (before)=0.566 mL, V_b (after)=0.556 mL.

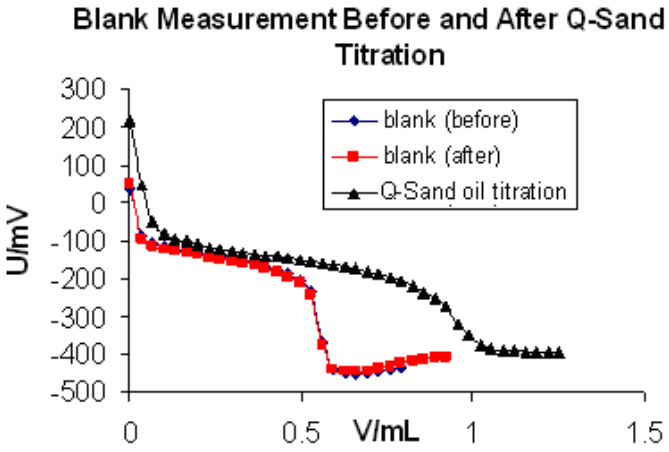

Figure 1-9. Blank measurements before and after Q-sand oil titration. Exposure to Q-Sand crude oil sample does not drastically change the electrode response. V_b (before)=0.557 mL, V_b (after)=0.554 mL

Note that Figure 1-8 shows a difference of 0.01mL (an error of 1.8%) between two blank titrations. This error would be significant if the acid number is low. In this case, oil sample size must be increased.

1.4.4 Effect of sample size, volume step, titration rate[4]

From equation 1-2, more accurate acid number value can be obtained by using larger sample size or smaller volume step. This is evaluated on MY8 crude oil sample by changing the sample size from 0.5 g to 1.0 g, the volume step from 0.02 mL to 0.05 mL. The effect of titration rate was evaluated by changing the dosage rate from 0.1 mL/min to 0.4 mL/min.

Table 1-2 shows that as sample size increased, standard deviation became smaller.

Table 1-2. Effect of sample size. ΔV=0.033 mL, titration rate=0.2 mL/min

Vi (mL)	Vb (mL)	Oil (g)	AN	Mean	Standard
0.687	0.528	0.5077	0.889	0.834	0.066
0.690	0.555	0.5037	0.761		
0.673	0.525	0.4934	0.852		
0.769	0.528	0.7543	0.907	0.907	0.040
0.735	0.486	0.7471	0.946		
0.724	0.497	0.7441	0.866		
0.798	0.497	1.0006	0.854	0.886	0.039
0.825	0.497	1.0024	0.929		
0.807	0.499	1.0004	0.874		

Table 1-3. Effect of volume step. Sample size=0.5 g, titration rate=0.2 mL/min

Vi(mL)	Vb(mL)	Oil (g)	ΔV(mL)	AN(mgKOH/gOil)	Mean	Standard Deviation
0.643	0.506	0.4912	0.020	0.796	0.835	0.048
0.646	0.504	0.4933		0.821		
0.660	0.507	0.4915		0.888		
0.687	0.528	0.5077	0.033	0.889	0.834	0.066
0.690	0.555	0.5037		0.761		
0.673	0.525	0.4934		0.852		
0.645	0.500	0.4990	0.050	0.829	0.784	0.098
0.642	0.525	0.4971		0.672		
0.648	0.500	0.4960		0.852		

Table 1-4. Effect of titration rate. Sample size=0.5 g, ΔV=0.033 mL

Vi(mL)	Vb(mL)	Oil (g)	Titration Rate (ml/min)	AN(mgKOH/gOil)	Mean	Standard Deviation
0.657	0.501	0.5017	0.1	0.883	0.875	0.046
0.668	0.502	0.5144		0.916		
0.662	0.518	0.4948		0.826		
0.687	0.528	0.5077	0.2	0.889	0.834	0.066
0.690	0.555	0.5037		0.930		
0.673	0.525	0.4934		0.852		
0.657	0.499	0.5046	0.4	0.889	0.829	0.073
0.645	0.515	0.4935		0.748		
0.657	0.506	0.5042		0.850		

Table 1-3 shows that as volume step decreased, standard deviation became smaller.

Table 1-4 shows that as titration rate decreased, standard deviation became smaller.

Take ½ ΔV as measuring accuracy, according to equation 1-2, this will change the accuracy in acid number by Error range $=1/2\Delta V \cdot M_w \cdot M / W = 1/2\Delta V \times 56.1 \times 0.05 / W$. Table 1-5 and 1-6 show that the standard deviation is smaller than the error range. The volume step and oil size adopted in these measurements satisfied accuracy requirement. Also, standard deviation becomes smaller with larger oil sample size (Table 1-2) and smaller volume step (Table 1-3), as expected. It is also found that accuracy improves with slower titration rate (Table 1-4).

Table 1-5. Error analysis by changing the oil size, ΔV=0.033 mL

Sample Size W (g)	0.5	0.75	1.0
Error range	0.093	0.062	0.046
Standard deviation	0.066	0.040	0.039

Table 1-6. Error analysis by changing the volume step, oil size=0.5 g

ΔV(mL)	0.020	0.033	0.050
Error range	0.056	0.093	0.14
Standard	0.048	0.066	0.098

1.4.5 Parallel blank

Every sample should have a parallel blank with same amount of organic solvent, because the organic solvent also consumes titrant and experimental result is shown below.

The blank solution was tested by changing the volume of the organic solvent as shown in Figure 1-10. The blank solutions have same amount of spiking solution (1ml), however, when the volume of the organic solvent increases, more TBAOH is used to get the inflection point. If we extrapolate the data to zero organic solvent, the titrant used is 0.38 ml (here, $C_{titrant}$=0.0526 M), which means the TBAOH and stearic acid is in stoichiometric ratio when no organic solvent presents. The organic solvent of the blank solutions consumes extra titrant, because IPA behaves as an acid when strong alkali is present.

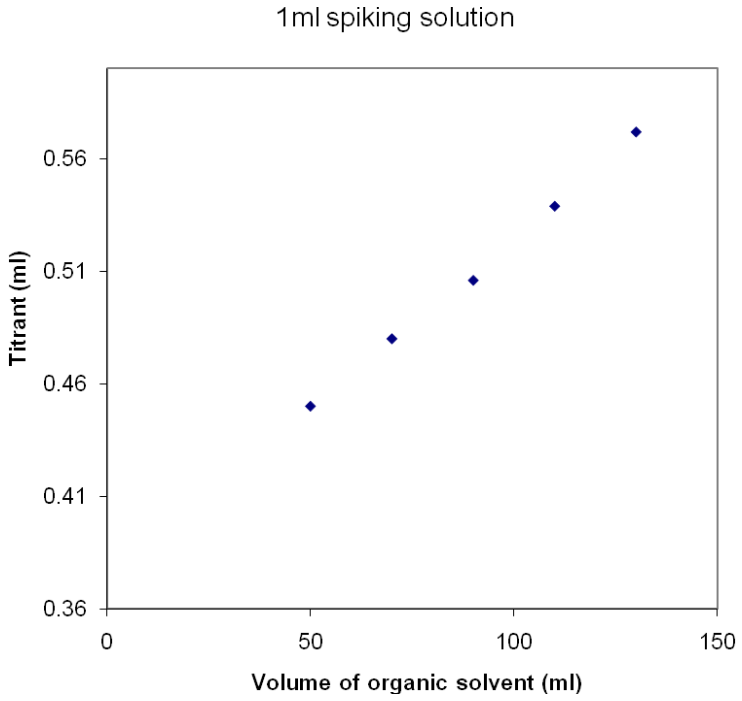

Figure 1-10. Volume of titrant used for blank solutions (1 ml spiking solution in the organic solvent with different solvent volume and titrant concentraton is 0.0526M)

1.4.6 Asphaltene precipitation

Pemex Akal oil precipitates with the standrd organic solvent during the titration as shown by Figure 1-11, so the organic solvent was changed to 70% toluene, 29.5% IPA and 0.5% DI water, because the solubility is enhanced by increasing ratio of toluene. Since the organic solvent is changed, the spiking method need to be checked. The new organic sovlents (toluene/ IPA ratio = 70/29.5) with spiking solution were studied and compared with the old organic solvents (toluene/ IPA ratio = 50/49.5) and results are shown by Figure 1-12 and 1-13, respectively.

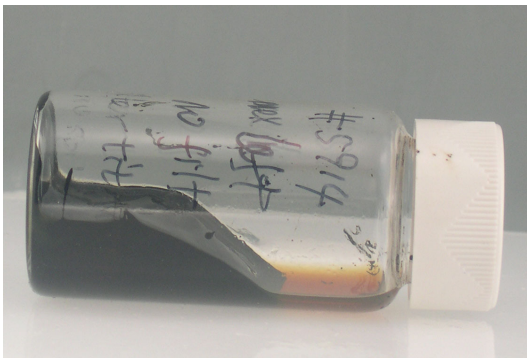

Figure. 1-11 Precipitate of 20g Pemex Akal crude oil with 1 ml spiking solution in 125 ml organic solvent (toluene/IPA=50/49.5)after titration.

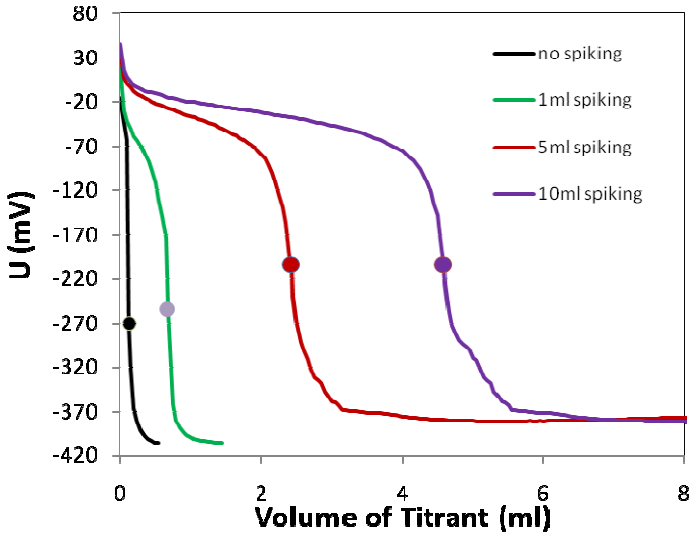

Figure. 1-12 Titration curves for 125ml new organic sovlents (toluene/ IPA ratio = 70/29.5) with 0, 1, 5 and 10 ml spiking solution

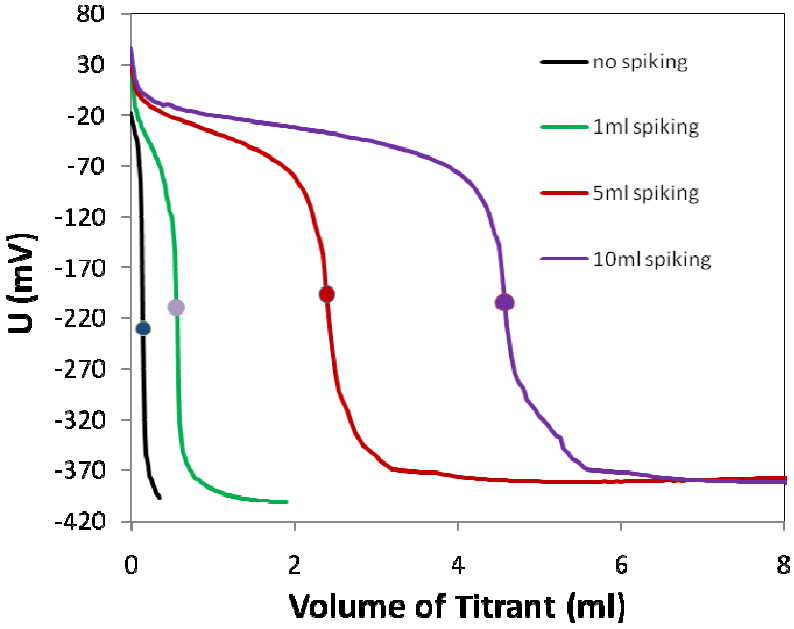

Figure. 1-13 Titration curves for 125ml standard organic sovlents (toluene/ IPA ratio = 50/49.5) with 0, 1, 5 and 10 ml spiking solution

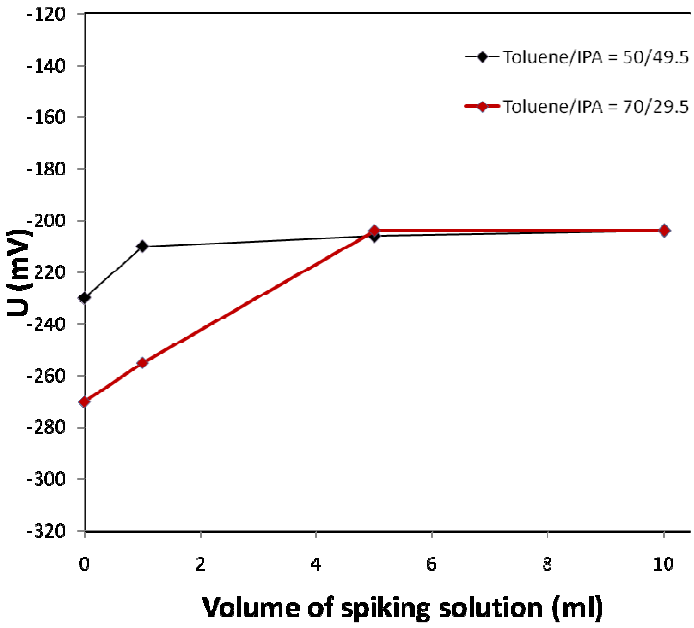

Figure. 1-14 Voltage at the inflection point of organic solvent (toluene/ IPA ratio: 70/29.5 and 50/49.5) with 0, 1, 5 and 10 ml spiking solution

From Figure 1-13 and 1-14, it is noticed that the voltage at the inflection point increase with increasing spiking solution volume. The voltage at the inflection point vs. spiking solution volume is plotted in Figure 1-14. Organic solvent with 50% toluene reach stable voltage with 1 ml spiking solution, however, organic solvent with 70% toluene needs 5 ml spiking solution to get stable voltage at the inflection point.

This is also observed in the titration results of Pemex Akal oil sample as shown in Figure 1-15. When 1 g Akal crude oil with 1 ml spiking solution is titrated, the effect of spiking is not enough, so the voltage at the inflection point for the sample and blank is very different. Also, the total acid number of Akal is very low (around 0.2 mgKOH/g), so inflection points for sample

and blank are close, which results in big system error. So sample size was increased to 10 g with 1 ml spiking solution, then the titration result gives multiple end points because the spiking solution is not enough. Then 5 g Akal and 5 ml spiking solution was titrated. this sample shows clear inflection point and the inflection points of sample and blank are found at simlar voltage.

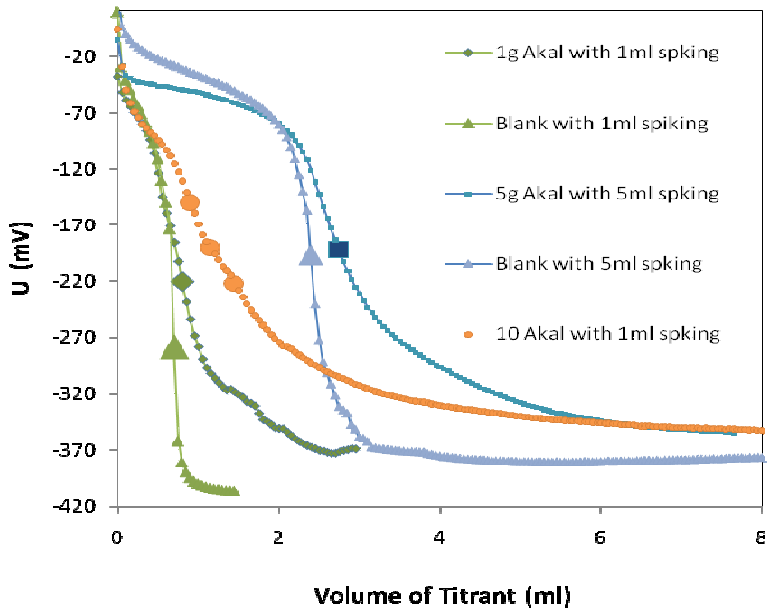

Figure. 1-15 Titration curve for Akal crude oil with different sample and spiking solution size in 100 ml organic solution (toluene/IPA=70/29.5)

1.4.7 Benefit of spiking method

With the ASTM standard procedure, it is sometimes ambiguous to choose the inflection point especially when a crude oil sample contains different acids with various pKa's. Such samples might give multiple inflection points, or these points off-set resulting in no inflection point. However,

spiking method allows titration using smaller oil sample and gives sharper inflection point as discussed in 1.4.6. (Figure 1-15).

The voltage at inflection point for sample and blank should be simlar; otherwise, the inflection point is not for carboxylic acid. For example, when MY8 is titrated by spiking method, as shown in Figure 1-16, a clear inflection point was shown around 160 mV, but the inflection point for the blank is around -210 mV, so the inflection point around 160mV is not the end point for carboxylic acid. A second inflection point was observed by continuous titration with more titrant. The first inflection point here indicates the Yates MY8 crude oil contains some strong acid, which can react with alkali, but does not produce soap. Therefore, spiking method helps to decide where the carboxylic acid inflection point is.

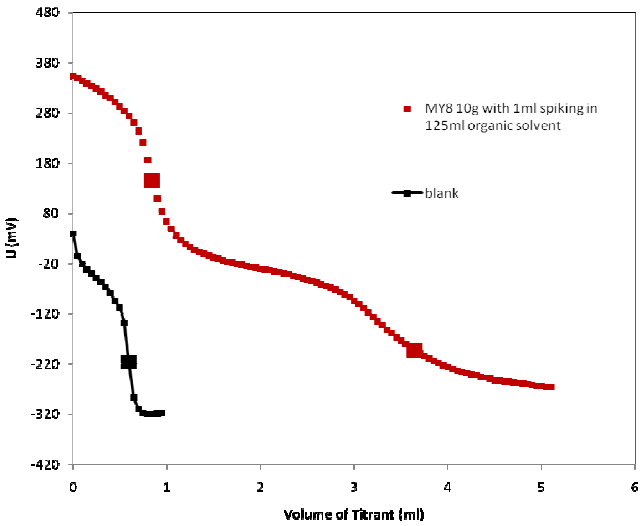

Figure. 1-16 10g Yates MY8 oil in 125 ml organic solvent with 1ml spiking solution

1. 5 Conclusions

Total acid number of crude oils is measured by acid-base titration. The spiking method by using stearic acid as blank gives clear carboxlic infletion point. There are different factors which affect the titration results, such as precondition procedure, electrode response, sample and spiking solution size, volume step, titration rate, parallel blank and asphaltene precipitation. All these parameters are studied in this manual to improve the titration technique.

1. 6 Reference

1. Fan, T., Buckley, J. S., "Acid Number Measurements Revisited", *SPE Journal*, 2007, 12(4), 496-500, SPE-99884-PA.
2. ASTM Standard Test Method D664-01 "Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration", Annual Book of ASTM standard, Sect. 5, Am. Soc. Testing Materials, Philadelphia, 2001.
3. http://www.metrohm.com
4. Robert Li's Ph.D. thesis.