

# SYSTEMATIC ERRORS IN MEASUREMENT OF MOISTURE BY KARL FISCHER METHODS

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*Abstract:* Studies on the moisture content of hydrocarbons and hydrocarbon mixtures indicate that the Karl Fischer methods typically used have systematic errors attributable to factory calibration of the coulometric instruments, improper setting of the operator adjustable parameters, and incomplete solubilization of hydrocarbons in the titration solvent. This study focuses on the solubility of the hydrocarbons in the titration solvent.

*Keywords:* Karl Fischer methods, hydrocarbons, systematic bias

## 1 INTRODUCTION

Two basic methods, volumetric and coulometric, utilize the Karl Fischer solvent system for the measurement of moisture. The primary advantage of the volumetric method is that it allows a wider latitude for vessel solvents, such as formamide, dimethylsulfoxide, chloroform:methanol 6:1 as well as methanol, and titrant composition such as the pyridine and imidazole based titrants. The coulometric method is more restricted as to the amount and type of cosolvent that can be added to the titration vessel but the water content is based solely on the physical principle of the Faraday equation which is used to calculate amount of water present, based upon the current used to convert iodide to iodine. Additionally the coulometric method is slightly more sensitive than the volumetric method. The accuracy of both Karl Fischer methods depends on: (a) the correct calibration of the instrument in the moisture range that the measurements are made, (b) the correct setting of the variable instrumental measurement parameters and the preset instrumental constants, (c) the availability of all of the water to the Karl Fischer reagent, and (d) the absence of side reactions that produce water as a product or react with iodine or iodide.

The assessment of systematic errors in the Karl Fischer measurement method requires the use of a suitable stable standard that can deliver a known amount of water accurately in the range of water content that the samples are expected to exhibit. Although water, oxalic acid, and potassium tartrate are routinely used as calibrants, they are not suitable below 1 mg of water. Many of the coulometric measurements, particularly those on oils, measure amounts of water levels of 10  $\mu\text{g/g}$  of sample and require calibration in the 50  $\mu\text{g}$  to 100  $\mu\text{g}$  range. We have shown that water saturated octanol (WSO) is stable and contains 41.2  $\mu\text{g}$  of water/ $\mu\text{L}$  of solution, thus permitting calibration from 41.2  $\mu\text{g}$  to >1000  $\mu\text{g}$  of water [1]. The concentration of the water in the WSO, both coulometrically and volumetrically, has been compared to that of oxalic acid and water saturated butanol [1] and it has been established by the method of standard additions [2].

WSO is compatible with the methanol based solvent systems. One to twenty five  $\mu\text{L}$  of WSO causes little change in the composition of the vessel solution. This standard provides a suitable material for the titration of the Karl Fischer solution used in the volumetric method and for the

verification of the coulometric instruments. The availability of a suitable standard permits the assessment of the systematic errors in the measurement of water by both the volumetric and coulometric methods of Karl Fischer water analysis.

There are three major sources of systematic error in the volumetric method: (a) the determination of the endpoint of the titration of small amounts of water, (b) the solubility of the sample in the vessel solution, and (c) the presence of side reactions. The measurement of small amounts of water by end point titration is inaccurate because the nonlinear approach to the constant rate of titrant consumption can comprise 30% of the titration curve [1]. The endpoint is usually determined at some point in the nonlinear segment of the titration curve and is detected by the absence of titrant addition for 10 seconds. This end point can occur at varying times during the nonlinear portion of the curve. Thus the titration may end prematurely, resulting in a negative bias. This bias can be circumvented by measuring the Karl Fischer reagent consumption graphically after the titrant addition has reached a constant rate [1]. Sample insolubility can result in a negative bias. (b) Side reactions such as the formation of methyl esters or the iodination of sulfhydryl groups [3,4] may give rise to a negative or positive bias. The transition from a homogeneous system to a heterogeneous or multiphase system as with oils [1] results in a negative bias, as some water is sequestered from the Karl Fischer reagent.

There are three major sources of systematic bias in the coulometric method: (a) the presetting of the instrumentally set constants, (b) the setting of the instrumental variables under the operator's control, and (c) the solubility and chemical reactivity of the sample [2]. There are two sources of bias associated with the constants preset in the instrument by the manufacturer. One is observed at water levels below 200  $\mu\text{g}$  and increases inversely with the water content. The other is associated with the incorrect setting of the end point of the instrument. This bias is a constant bias that may be associated with the incorrect electronic setting of the numerical value for the Faraday constant or some other constant. The bias associated with the operator dependent variables consists of the proper setting of the rate of titration (end drift) at which the titration process stops and the setting of the time at which the rate of titration remains below the value set for the end drift. The third type of bias is associated with the well-documented chemical reactivity of analytes such as aldehydes, ketones, organic acids, and sulfhydryl groups [3] and with the solubility of analytes such as hydrocarbons and oils.

The purpose of this paper is to review some of the aspects of the sources of systematic errors in the measurement of moisture by the Karl Fischer methods and to extend our observations on the effect of solvent composition on the solubility of oils and its effect on the titration of water in these materials.

## 2 EXPERIMENTAL

The Voltesso oils were obtained from Insoil Canada Ltd. Calgary, Canada and the Teresstic oils were obtained from Trico Mfg. Corp., Pewaukee, WI. The xylene, hexane, petroleum ether, kerosene, and Drakeol oils (Fisher Scientific, Pittsburgh, PA) were saturated with water. All other methods and materials have been described elsewhere [1,2].

### 3 RESULTS

The evaluation of the systematic bias observed in the measurement of water in transformer oils [1] has been extended to higher viscosity oils, such as mineral oils and hydraulic oils. This bias is characterized by the apparent inability to titrate water in an oil sample that is added to the volumetric titration vessel at the point that the solution undergoes a transition from a homogenous solution to a heterogeneous mixture. Figure 1 illustrates that this phenomenon is also observed for hydraulic oils. In both cases the reagent consumption by the WSO water standard (solid squares) in each individual series of titrations (as in Figure 1A or 1B) was constant while the

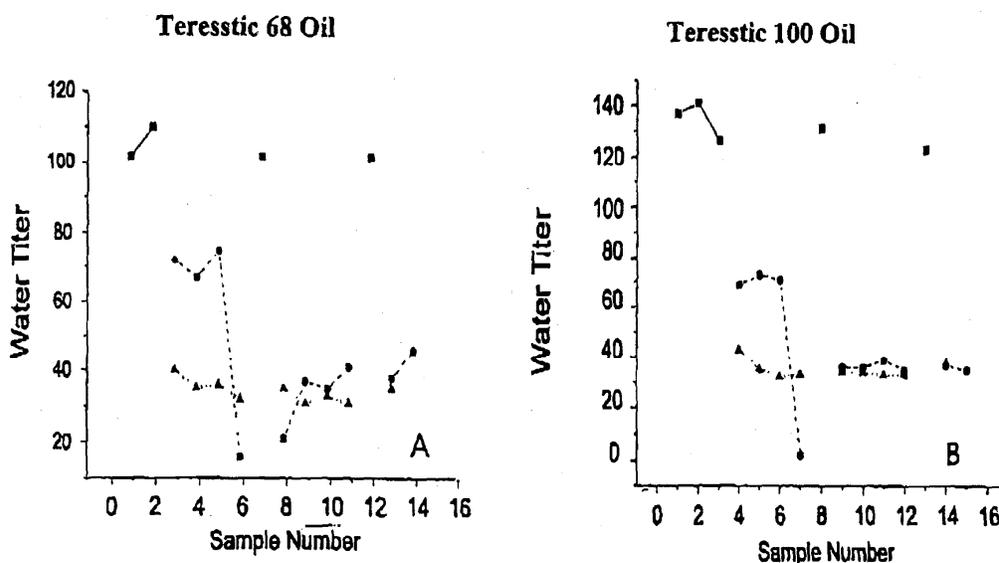


Figure 1. Sequential titration of water in hydraulic oil samples and WSO. The solid squares represent the WSO samples (10  $\mu$ L); response is in mm of chart distance. The solid circles represent the titration of the oil by the volumetric method using the pyridine reagent (chloroform concentration 73-76 vol.%) and the solid triangles represent the titration of the oil by the coulometric method using the one compartment cell and the Coulomat AG-H); response is in  $\mu$ g of water/g oil. The transition from a homogeneous to a heterogeneous solution occurred between samples 6 and 7. The water titer for each oil sample is in mg/kg of oil and for the WSO in mm of chart distance.

reagent consumption of the oils decreased dramatically at the time of transition from a homogeneous to a heterogeneous solution (80% for the Teresstic 68 oil and 100% for the Teresstic 100 oil). Additionally, in the Teresstic 68 oil experiment (Figure 1A) the amount of water measured in the WSO remained unchanged in spite of the fact that the oil samples titrated immediately before and after the WSO samples were observed to have low concentrations of water. Thus it is the oil that causes the sequestering of the water, but the system can completely titrate water that is not associated with the addition of an oil sample using the volumetric method. The water measured in the oil increases slightly as succeeding samples are titrated but remains lower than that observed before the phase transition. The universality of this phenomenon is illustrated in the combined data in Tables 1-3. This phenomenon is observed with both the

imidazole (Hydranal-Composite) and the pyridine buffered titrants. For some oils at very high chloroform concentrations the voltage across the indicator electrode breaks down before the phase transition occurs (i.e the end point is not detected and the addition of titrant does not stop). As the *initial* chloroform level in the vessel solution is reduced a greater number of different oils

Table 1. Comparison of the waters measured by the two volumetric methods.

Karl Fischer Reagent CHCl <sub>3</sub> (vol%) <sup>a</sup> Sample <sup>b</sup>	Hydranal Composite 2 66-70		Pyridine 73-76
	Water µg/g (SD, N) <sup>c</sup>	Water µg/g (SD, N) after precipitate formed <sup>d</sup>	Water µg/g (SD, N)
Xylene	409 (12, 9)		382 (12, 9)
Hexane	98 (6, 6)	116 (7, 3) <sup>d</sup>	95 (7, 6)
Petroleum Ether	92 (4, 3)	108 (2, 3) <sup>d</sup>	87 (7, 10)
Kerosene	109 (5, 5)		102 (4, 5)
Univolt N61	45 (7, 5)		40 (3, 16)
Coray 22	73 (5, 6)		77 (5, 18)
Drakeol 13	73 (n.a., 2)		85 (6, 9)
Drakeol 35	83 (n.a., 2)		76 (6, 9)

<sup>a</sup> The vol. % of chloroform in the titration vessel solvent after the solvent was titrated to dryness

<sup>b</sup> The size of each sample varied between 1.5 and 3 g

<sup>c</sup> The SD represent the standard deviation of a single measurement, N the number of samples measured, n.a.= not available

<sup>d</sup> a precipitate, which most likely is imidazole, was observed in only these two sets of titrations

Table 2. Comparison of the water measured by the two coulometric methods.

Vessel Type <sup>a</sup> Karl Fischer Reagent	Diaphragmless Coulomat AG-H		Diaphragm Coulomat A + CG	
	Clear Solution	Cloudy Solution	Clear Solution	Cloudy Solution
Sample <sup>c</sup>	Water µg/g (SD, N) <sup>b</sup>			
Xylene	389 (13, 7)	n.o.	389 (10, 12)	n.o.
Hexane	75 (4, 8)	n.o.	70 (7, 9)	n.o.
Petroleum Ether	81 (2, 11)	n.o.	74 (8, 9)	n.o.
Kerosene	77 (4, 9)	54 (2, 4)	82 (2, 3)	81 (1, 6)
Univolt N61	46 (7, 3)	44 (6, 3)	n.o. <sup>d</sup>	18 (2, 12)
Coray 22	66 (6, 3)	63 (3, 5)	n.o.	49 (4, 12)
Drakeol 13	n.o.	47 (5, 9)	n.o.	48 (7, 12)
Drakeol 35	n.o.	50 (5, 9)	n.o.	34 (2, 9)

<sup>a</sup> The diaphragm titration vessel contains two compartments (anode and cathode) separated by a porous frit. The other titration vessel consists of a single compartment containing both the anode and the cathode.

<sup>b</sup> The SD represent the standard deviation of a single measurement and N represents the number of samples measured

<sup>c</sup> The size of each sample varied between 1.5 and 3 g

<sup>d</sup> n.o. = not observed

undergo this phase transition. For water saturated oils (Drakeol and Teresstic oils) the measured water decreases to a constant level (Tables 2 and 3) while the measured water of the WSO remains constant through the entire titration sequence (Teresstic oils, Figure 1). Previous studies [1] and Table 3 show that the coulometric water content is essentially identical to the volumetric water content after the transition point has been passed. This observation is true for both the water unsaturated oils and the water saturated oils and the universality of this observation can be seen when the volumetric values in Table 1 are compared to the coulometric values in Table 2. Furthermore, the water measured in the Univolt N61 oil are the same for the volumetric measurements and the coulometric diaphragmless vessel. A comparison of the results obtained using the diaphragm vessel to those using the diaphragmless vessel indicate that different oils give different results with each method before and after the formation of a heterogeneous system, but no well-defined trend has been identified.

Table 3. Comparison of the volumetric and coulometric water titers measured in water saturated and unsaturated hydraulic fluids.

Method	Volumetric			Coulometric Diaphragmless Cell Coulomat AG-H
	Pyridine 73-76			
Karl Fischer Reagent CHCl <sub>3</sub> (vol%) <sup>a</sup>	Water µg/g (SD, N) <sup>b</sup>			
Solution State Sample	Clear	Transition	Cloudy	Cloudy
<b>Water Unsaturated<sup>c</sup></b>				
Teresstic 68	80 (10, 4)	n.o. <sup>d</sup>	n.o.	34 (3, 9)
Teresstic 100	68 (4, 4)	0	40 (4, 7)	35 (4, 10)
Teresstic 100 SHP	94 (17, 4)	0	51 (1, 4)	53 (4, 9)
Royal purple	230 (12, 4)	135	161 (10, 5)	
<b>Water Saturated</b>				
Teresstic 68 <sup>e</sup>	248 (5, 6)	143	208 (3, 4)	186 (11, 9)
Teresstic 100 <sup>f</sup>	615 (16, 10)	466	538 (13, 5)	516 (16, 11)
Teresstic 100 SHP <sup>f</sup>	1466 (39, 6)	1373	1369 (26, 5)	1359 (22, 9)

<sup>a</sup> The vol. % of chloroform in the titration vessel solvent after the solvent was titrated to dryness

<sup>b</sup> The SD represent the standard deviation of a single measurement and N represents the number of samples measured

<sup>c</sup> The size of each sample varied between 1.7 and 2.2 g

<sup>d</sup> n.o. = not observed, 0 indicates that no water was measured in the oil sample assayed at the transition point

<sup>e</sup> The size of each sample varied between 1.6 and 1.8 g

<sup>f</sup> The size of each sample varied between 0.8 and 0.9 g

All tables list the hydrocarbons and hydrocarbon mixtures (except for xylene) in order of increasing molecular weight distribution and viscosity. The number of samples that can be titrated with Hydranal Composite 2 before the occurrence of the transition to a heterogenous system decreases as both the weight distribution and viscosity increase. Additionally, the water unsaturated, low viscosity Teresstic oil in the presence of the pyridine buffered titrant causes a breakdown of the voltage of the indicator electrode before the transition can occur, whereas two high viscosity Teresstic oils undergo a simultaneous transition to a heterogeneous mixture and

to a reduction in the measured water. This cannot be explained as a function of water content because all three oils have nearly identical water contents and that of Teresstic 100 (viscosity = 100 cSt, 40 °C) is lower than that of Teresstic 68 (viscosity = 68 cSt, 40 °C). It is also significant that the water content for xylene is essentially the same by all four titration procedures and that hexane and petroleum ether do not undergo a phase transition, but the water measured by the coulometric methods is lower than that obtained by the volumetric methods.

Examination of the relationship of the volumetric results to the coulometric results reveals that in most cases the water measurements obtained coulometrically were equivalent to the measured volumetrically under heterogenous conditions (Table 4). This was not true for the low molecular weight low viscosity materials such as xylene, hexane, and petroleum ether because they never formed a heterogeneous mixture. In the case of the Univolt N61 oil, this decrease in measured water was observed only for the diaphragm vessel when the solution became heterogeneous upon addition of the first oil sample. In the case of Coray 22 oil, the water measured using the

Table 4. Summary of the water titration patterns of hydrocarbons and hydrocarbon mixtures using the Karl Fischer methods.

Method	Volumetric					Coulometric					
	Pyridine		Hydranal Composite 2			Diaphragmless			Diaphragm		
Karl Fischer Reagent	73-76		66-70			Coulomat AG-H			Coulomat A + CG		
CHCl <sub>3</sub> (vol%) <sup>a</sup>	1	2	1	2	3	1	2	3	1	2	3
Solution State <sup>b</sup>	1	2	1	2	3	1	2	3	1	2	3
Sample <sup>c</sup>	Water (µg/g) <sup>d</sup>										
Xylene	382	n.o. <sup>e</sup>	409	n.o.		389	n.o.		389	n.o.	
Hexane	95	n.o.	98	n.o.		75	n.o.		70	n.o.	
Petroleum Ether	87	n.o.	92	n.o.		81	n.o.		74	n.o.	
Kerosene	102	b	109	11	b	77	71	54	82	82	81
Univolt N61	40	b	45	b		46	44	43	n.o.	n.o.	18
Coray 22	77	b	73	5	45	66	64	63	n.o.	n.o.	49
Univolt 60 <sup>e</sup>	n.a.		46	b		18			n.o.	n.o.	9
Diala A <sup>c</sup>	n.a.		54	0	26	19			n.o.	n.o.	17
Drakeol 13	85	b	73	47	43	n.o.	n.o.	47	n.o.	n.o.	48
Drakeol 35	76	b	83	49	51	n.o.	n.o.	50	n.o.	n.o.	34

- <sup>a</sup> The vol. % of chloroform in the titration vessel solvent after the solvent was titrated to dryness
- <sup>b</sup> 1 = clear solution, 2 = transition point, 3 = two phase mixture. Each value under state 1 or 3 represents a mean of 4 - 10 measurements. The transition values (solution state 2) represent a single measurement and 0 indicates that no water was detected in that oil sample.
- <sup>c</sup> The size of each sample varied between 1.5 and 3 g
- <sup>d</sup> The means of the water content of this oil represents the average of two groups of 5 samples each. All samples were analyzed under single phase conditions
- <sup>e</sup> n.o. = not observed, b = breakdown of voltage across indicator electrode, n.a. = not analyzed

diaphragmless vessel was midway between the volumetric water content observed under homogenous conditions and that observed under heterogenous conditions. The water content under heterogeneous conditions using the diaphragm vessel was equal to that obtained

volumetrically under heterogenous conditions. In the case of the higher viscosity oils (Drakeol oils, Tables 2 and 4, and Teresstic oils, Table 3) the coulometric results were always equal to the water content obtained volumetrically in heterogeneous solutions. These results suggest that a graded response occurs as a function of the molecular weight distribution and viscosity. This phenomenon is not a function of the saturation level of the water in the oils nor of the amount of water in a given oil since it is observed under a wide variety of saturation levels and water content.

There is no consistent explanation for the variation between the results obtained by the two different coulometric methods. It is clearly not an electronic problem because the same electronic components were used for both sets of measurements. Thus, the discrepancies in water content of a given sample must be due either to a solvent effect, a titration vessel effect, the hydrocarbon composition of the sample or some combination thereof. These results are consistent with the results reported using a diaphragmless cell by Cedergren and Lundstrom[5].

#### 4 DISCUSSION

This study addresses the relationship of variable amounts of water obtained by different methods to (a) the composition and viscosity of the hydrocarbons and hydrocarbon mixtures and (b) the disposition of titratable water after the vessel solution undergoes a transition to a multiphase heterogeneous suspension. Four different titration systems were used. Two were volumetric methods, one using a pyridine-buffered titrant and the other using an imidazole-buffered titrant. Two were coulometric methods one using a diaphragmless vessel with a pentanol-based solvent and the other using a diaphragm vessel with a chloroform-based anodic solvent.

The key to understanding the discrepancies in the titer of moisture in oils in general, and in transformer oils in particular, was the observation that the volumetric moisture titer of the oil sample was higher when it was completely dissolved in the vessel solvent than when it formed a heterogeneous suspension. This was most pronounced in the presence of a large amount of chloroform [1]. As samples were sequentially added to the vessel solvent it underwent a transition from homogeneity to heterogeneity. At the transition point in many cases very little water was measured (Table 4). This was most evident in oils that were not saturated with water. Under the same conditions the water measured in WSO was unaffected by the transition to a heterogeneous system (Fig.1) yet the water, that was titrated in oil samples before and after the measurement of the water in the WSO was abnormally low. This is consistent with the sequestering of the water in the oil sample when the oil was redistributed into the second phase. As much as 50% of the water can be sequestered from every water unsaturated sample after the transition point has been passed. When the oil is saturated with water the very low titer at the transition point is not observed but the measured water is reduced by a significant amount as in the water-saturated Drakeol and Teresstic oils. This is also consistent with the sequestering of a fraction of the water by the oil in one of the phases. The sequestering is rapid and this water is no longer accessible to the Karl Fischer reagent. The factors that control the amount of water that is sequestered remain to be evaluated.

Previous studies with WSO [1,2] revealed a dependence both on the solvent and on the design of the titration vessel. The results summarized herein indicate the occurrence of two additional

trends that are related to the molecular weight distribution of the hydrocarbons comprising the oils: (a) the graded response within a single method as the molecular weight of the component hydrocarbons increases and (b) the differential response of the different methods of Karl Fischer analysis to a given oil. The graded response is evident in both the volumetric and coulometric methods. This response is characterized by the absence of a two phase system and a breakdown of the voltage across the indicator electrode. This progresses first to the appearance of the breakdown of the voltage across the indicator electrode and then to the replacement of the breakdown of the voltage by the transition to a heterogeneous (multiphase) system characterized by a reduction in the amount of measured water. This transition occurs at a lower molecular weight distribution with the imidazole (Hydranal) titrant than with the pyridine titrant. In the case of the coulometric methods a homogeneous vessel solution is observed only with the first few samples of the low molecular weight samples. With all other hydrocarbon mixtures only a heterogenous solution is observed when the oil sample is introduced. The water content is about 50 % of that measured by the volumetric method when the volumetric titration-vessel solvent is homogeneous, with the exception of kerosene, Univolt N61, and Coray 22 oils. In addition to the graded response as a function of the molecular weight distribution and viscosity of the sample, the water measurements obtained by the two volumetric methods are close to each other for a given oil sample. In contrast, the water content obtained by the coulometric methods do not always agree and may or may not be similar to those obtained by the volumetric method. For xylene, the most polar of the samples tested, all four methods measured a similar amount of water. For all other oil samples the coulometric water measurements are significantly lower than the volumetric values with the exception of Univolt N61 oil measured using the diaphragmless vessel. With some oils (Univolt oils) the water measured using the diaphragmless vessel was lower than that obtained with the diaphragm vessel. The basis of this observation remains unexplained. The relationship between the amount of water measured by the volumetric and the coulometric methods appears to be independent of the level of saturation of the oil sample and the amount of water in the sample. However, the measurement of very low amounts of water is observed only when the oils are not saturated with water.

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Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that equipment or material is necessarily the best for the purpose.

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