MODIFICATION OF KARL FISCHER METHOD FOR DETERMINATION OF WATER IN LIGHT PETROLEUM PRODUCTS INCLUDING AVIATION FUELS

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Classical Karl Fischer method has been modified so as to make it suitable for determining free and dissolved water present in aviation fuels in excess of 10 ppm which is considered as limiting concentration value for safe fueling of aircrafts particularly in the arduous climatic conditions as encountered in military operations. The modified method employed a special ethylene glycol solvent mixture and another water-saturated fuel sample as blank.

Presence of dissolved and suspended water in aviation fuel oils, even in minute quantities, markedly increases filtration troubles since the ice crystals formed at freezing temperature cause plugging of filters. Besides operational difficulties, gum formation and corrosion are stimulated causing error in determination of other fuel-properties. Undissolved water as a contaminant gives rise to a two-phase system in aviation fuels in which water is found suspended generally in excess of 30 ppm.

Karl Fischer titration method[1] has been used in the past to determine total water in the range of 50–1000 ppm. An oil sample is titrated with standardised Karl Fischer Reagent, (KFR, solution of iodine and sulphur dioxide in pyridine) to end point indicated by reddish colour due to iodine (eqn. 1). Materials like alkalies, oxidising and reducing agents mercaptans and some nitrogenous substances which react with iodine, therefore, cause interference to end point.

$$I_2 + SO_2 + 3C_2H_5N + H_2O + ROH = 2C_2H_5N.H_7 + C_2H_5N.HSO_4.R \ldots\ldots\ldots (1)$$

However, due to dissimilar conditions of water concentration prevailing during standardisation of KFR in presence of methanol and during titration of oil sample, the accuracy is decreased. In proposed modification, methanol was replaced with a mixture of ethylene glycol, which showed better results, and oil sample itself in equal volume. A sample of water saturated oil was taken as blank for determination of free water separately. The simple modified method gave acceptable accuracy of 2-4 ppm, within 100 ppm range, as compared to 15 ppm found with original method (Table 1).

Table 1

Total moisture in aviation turbine fuel (ATF) samples as determined by modified method

Samples	Water content, ppm				Min and max variation ppm
	1	2	3	4	
ATF-1 (As received)	9·8	8·7	8·0	9·2	0·6–1·8
ATF-2 (wetted)	39·4	40·5	42·5	41·6	0·9–3·1
ATF-3 (wetted)	100·2	96·1	98·7	99·8	1·1–4·1

METHOD FOR DETERMINATION OF TOTAL WATER

(*a*) *Standardisation of KFR solution*: Ethylene glycol and given oil sample, 25 ml each, were taken in a clean, dry titration flask which was then closed immediately with air-tight stopper. In order to accumulate water in glycol layer and to make end point sharper, the contents of flask were stirred for two minutes on a magnetic stirrer, KFR solution was added from an automatic delivery type burette graduated in 0·01 ml, with stirring all through first in increments of 0·1 ml and at close of end point 0·05 ml. End point was marked when a reddish colour persisted in glycol layer for half a minute.

Now an amount of distilled water equal to that of expected water content in oil sample taken was added with help of a micro-syringe capable of dispensing upto 10 mg of water. Stirring was revived to mix the extraneous water thoroughly. The mixture was reteirated with KFR solution to end point. Volume of KFR solution consumed was recorded disregarding the amount used in previous titration.

(*b*) *Titration of oil sample*: Ethylene glycol and oil sample, 25 ml each were taken in a fresh flask and water was neutralised with KFR solution as done before but without adding any extraneous water. In this mixture 100 ml of oil sample was added and titrated immediately with KFR solution with constant stirring. Volume of KFR solution consumed was recorded disregarding the previous consumption.

Calculation:

$$\text{Water, ppm, as received} = \frac{10 \times \text{mg water added in glycol+oil mixture} \times \text{ml KFR solution used in titration of 100 ml oil sample}}{\text{ml KFR solution used in standardisation of KFR}}$$

DETERMINATION OF FREE WATER

The KFR method was used to detect undissolved water in the same manner as described for total water except that a sample of water-saturated fuel oil was taken as blank. In order to saturate the fuel with water a stock sample consisting of one litre oil was taken in a closed vessel containing a thick round filter paper wetted with water. The oil was then allowed to stand at constant temperature for a day. The test sample was siphoned from stock sample without agitating or exposing it to atmosphere. Titration was carried out in similar way as for total water.

REFERENCE

1. ASTM Standards D. 1744-64.