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BROMINE NUMBER DETERMINATION OF PETROLEUM DISTILLATES BY THERMOMETRIC TITRATION. COMPARISON WITH OTHER METHODS

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ABSTRACT

The bromine number determination of petroleum distillates by thermometric titration is compared with the official colour-indicator and electrometric titration methods. A substantial advantage of the thermometric technique is that it is not necessary to regenerate the transductor, which can be handled without any special care.

INTRODUCTION

The bromine number is used for determining some impurities, basically olefinics, in petroleum distillates. In some petroleum distillates, p.e. aviation fuels, etc., the basic controls are tests directly and indirectly related to energy content and combustion characteristics. Determination of olefinic components is directly connected to these concepts [1].

Olefin content of several petroleum distillates is limited by specification, implying that these distillates are obtained by blending straight-run distillate components, virtually free of olefins. The olefin content is usually determined by the ASTM test for hydrocarbon types in liquid petroleum products by fluorescent indicator adsorption [2], although olefins in some specifications are controlled by the ASTM test for bromine number of petroleum distillates [3,4].

Technically, the bromine number is the number of grams of bromine reacting with 100 g of the sample under prescribed conditions. By this definition, bromine consumed by addition, substitution, oxidation and reaction with sulfur, nitrogen and oxygen-containing compounds is included in

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TABLE 1

90% Distillation point [8]	Bromine number maximum
Under 205°C	100
205 to 327°C	10

the bromine number and the estimation of olefinic unsaturation depends on the rate and thoroughness of the addition reaction. The addition of bromine proceeds readily at temperatures as low as 0°C or below. Decreasing temperature, time of contact, or concentration of free bromine tend to delay both substitution and oxidation reactions. Other factors, such as solvent medium, agitation, and exposure to actinic light, also affect the rate of some reactions. Therefore the conditions of bromine number tests are usually established on an empirical basis to give reasonable values with representative materials [4]. Thus we can observe that the results obtained by the colour-indicator method (back titration method) [3] are higher than those obtained by direct electrometric titration [4].

Normally these methods can be applied to gasoline (including lead fuels), kerosene, and distillates in the gas oil range which fit between the limits shown in Table 1, although not when blending agents such as alcohols, ketones, ethers, or amines are present. For pretroleum hydrocarbon mixtures with a bromine number of less than 1.0, a more precise measure of bromine-reactive constituents can be obtained by using other test methods [5–7]. In this paper, we compare the official methods [3,4] with the proposed direct thermometric titration for bromine number determination.

EXPERIMENTAL

Colour-indicator method [3]

The sample, dissolved in 1,1,1-trichloroethane, is treated at room temperature with an excess of bromide–bromate solution in the presence of glacial acetic acid. The excess of bromine is reduced with potassium iodide and the liberated iodine determined by sodium thiosulphate. The sample size depends on the bromine number, and can vary between 0.5 and 20 g.

Reagents used are: 1,1,1-trichloroethane, glacial acetic acid, sodium thiosulphate 0.1 N, potassium iodide solution 150 g l^{-1}, starch solution 0.5%, potassium bromide–bromate solution 0.5 N.

Direct electrometric titration method [4]

The results are obtained by the method of ref. 3 and transformed to those of the method from ref. 4 by the equation described in ref. 3.

The relationship between the bromine number of straight-run gasolines, cracked gasolines, commercial gasolines, kerosenes, and light gas oils, determined by the colour-indicator method [3] and the electrometric method [4] is approximate and expressed by

$$A^{1/3} = 1.012(B)^{1/3} + 0.135$$

where A = bromine number determined by method in ref. 3 and B = bromine number determined by method in ref. 4.

Direct thermometric titration method

A know weight of the sample, direct or dissolved in hexane, is titrated with standard bromide–bromate solution in acetic acid medium. The end-point is indicated by a sudden change in the thermometric titration curve when free bromine appears. For each titration 1 ml of the sample or 0.5 ml of its solution in hexane is used (depending on its bromine number) together with 65 ml of 85% acetic acid (0.5 N solution in both potassium bromide and bromate).

The apparatus is the same as that described in previous reports [9,10]. A thermistor of the thermometer type with 100 kΩ of nominal resistance value at 25°C was selected. Titrant was added by a Radiometer ABU 12 auto-burette, with a 5 ml cylinder. Speed reagent addition was 0.710 ml min^{-1}, register speed 3 cm min^{-1}, and sensitivity 50 mV, which corresponds to 0.02°C cm^{-1}.

RESULTS

The shape of the thermometric curves is greatly affected by acetic acid concentration. As is shown in Fig. 1, blank determinations present very different thermometric curves, when different acetic acid concentrations are used. Best conditions are obtained with 85% acetic acid, and this concentration was used in further experiments.

The thermometric titration curve for bromine number presents four different intervals. The first is due to endothermic bromine formation, the second to exothermic bromation of the sample, and the third zone, with a lower slope than the seond, indicates less exothermic dilution of the residual free bromine. The fourth zone begins when the bromide–bromate addition is stopped, thus corresponding to the base-line. A thermometric curve is presented in Fig. 2.

In Table 2 a comparison between theoretical and experimental values for the bromine number of several pure compounds by thermometric and electrometric titration [4] is showm. It can be observed that the experimental bromine numbers obtained by thermometric titration are lower than the

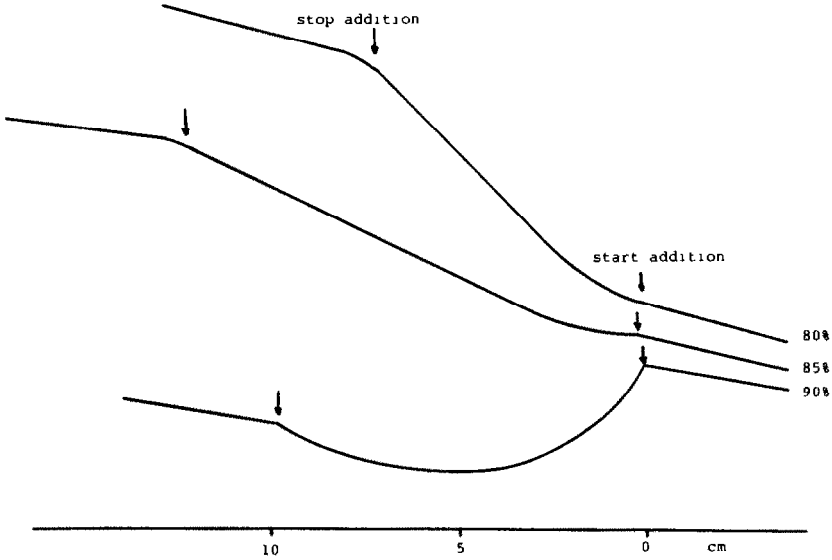

Fig. 1. Blank determination using diferent concentrations of acetic acid.

theoretical values, opposite to the observations made by the electrometric method. In both methods the error values are similar. In Fig. 3 the thermometric curves for these compounds are represented.

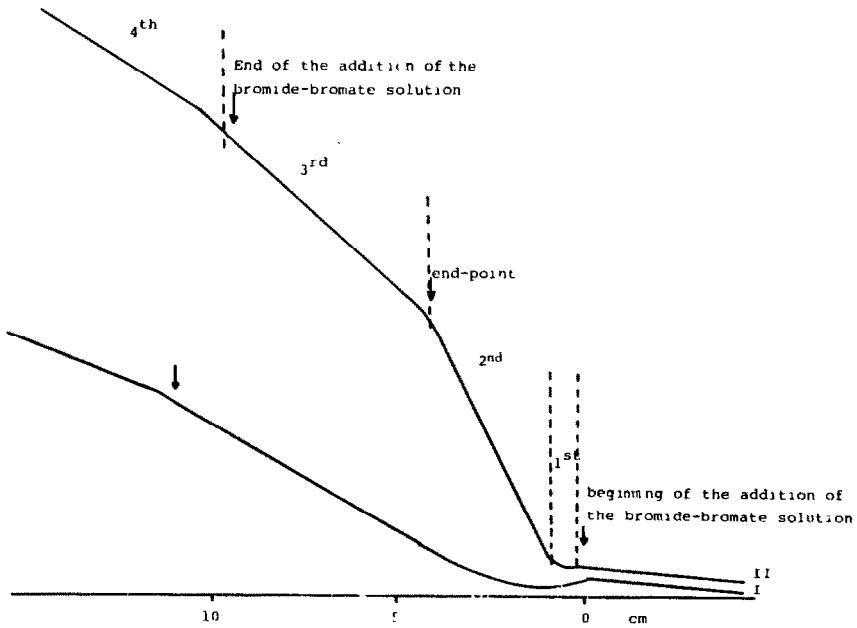

Fig. 2. Thermometric curves of a blank (I) and distillate No. 3 (II).

TABLE 2

Bromine number determination of the standards

Compound	Theoretical bromine number	Thermometric titration		Electrometric titration [4]	
		Experimental	Error(%)	Experimental	Error(%)
1-Hexene	189.9	200.3	5.5	181.0	−4.7
1-Heptene	162.8	174.5	7.2	136.0	−16.6
1-Octene	142.4	150.1	5.4	132.0	−7.0
Cyclohexene	194.6	197.6	1.5	193.2	−0.7

In Fig. 4 the thermometric curves for several petroleum distillates of different origin are shown. The bromine numbers are listed in Table 3. Results obtained by the direct methods, electrometric titration (calculated) and by thermometric titration are similar, but lower than those obtained by the colour-indicator method. As discussed previously, in the last method the bromine number measures not only the addition reaction, but also substitution and oxidation reactions.

As is shown in Table 3, bromine number is useful to distinguish straight-run petroleum distillates from those of other origin.

Thermometric titration compares well with standard methods for the speed of its analysis, precision and independence from distillate characteristics. A substantial advantage of the thermometric technique is that the transducer is isolated from the sample solution by means of the glass sheath,

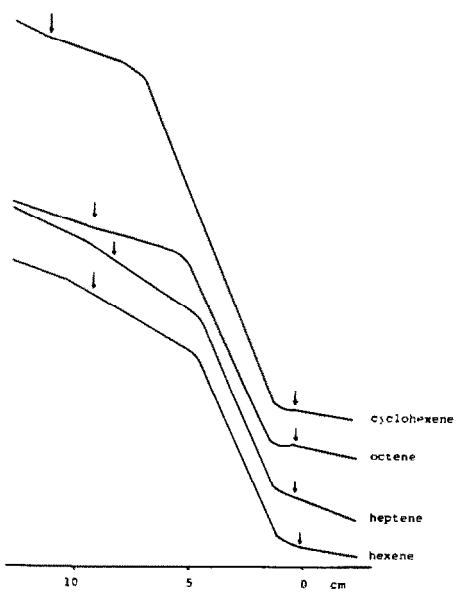

Fig. 3. Thermometric curves for several pure compounds.

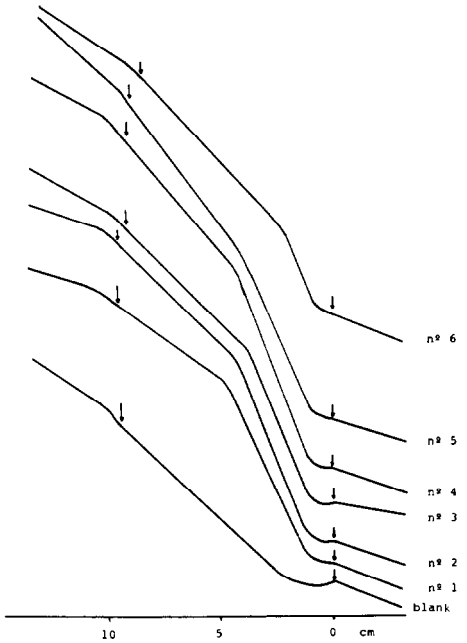

Fig. 4. Thermometric curves for several petroleum distillates.

TABLE 3

Bromine number determination of the petroleum distillates

Petroleum distillates [a]	Concentration ($g\,l^{-1}$)	Colour-indicator method [3]	Electrometric titration [4]	Thermometric titration
1	62.8	110.6	97.96	96.8 ± 1.1
2	89.5	92.0	81.04	80.8 ± 0.8
3	320.1	20.0	16.6	16.3 ± 0.9
4	618.1	13.2	10.68	10.4 ± 0.7
5	869.2	6.7	5.17	5.0 ± 0.6
6	739.2	2.9	2.08	2.3 ± 0.3

[a] Petroleum distillates 1 and 2 visbreaking origin; petroleum distillates 3, F.C.C. origin; petroleum distillates 4, 5 and 6, straight-run origin.

which avoids poisoning, inactivation, etc., and therefore regeneration or any other special care is not necessary.

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