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F.K.F.S. Method for the Determination of the Bromine Content in Aviation Fuels

Author - O. Widmaier

SYNOPSIS: According to the technical specifications for aviation fuels and their constituents, the freezing point of the fuel should not be above -60°C. This condition is not always met. At considerably higher temperatures, the ethylene bromide added to leaded fuels to prevent lead oxide formation separates as crystals; this may result in dangerous lead deposits producing corrosion in the combustion chamber.

It is therefore necessary for the bromine content of aviation fuels to be rapidly determined from time to time; this can be done with the method described below.

CONTENTS:

I - AIM AND SCOPE OF THE TESTS.

The anti-knock value of aviation fuels is increased by additions of up to 0.125% by volume of T.E.L.; in the combustion chamber this is transformed into lead oxide, producing serious corrosion. The decomposition of T.E.L. to lead oxide[1),2)] is prevented by adding ethylene bromide; in the presence of atmospheric oxygen and under certain temperature and pressure conditions the following chemical reaction takes place :-

$$Pb(C_2H_5)_4 + (CH_2)_2Br_2 \xrightarrow{16O_2} PbBr_2 + 10\,CO_2 + 12\,H_2O$$

The resulting lead bromide has a melting point of 370°C., and is therefore considerably more volatile than lead oxide (melting point 800°C), thus minimising lead deposition in the engine. However, having a melting point of 8°C., ethylene bromide tends to separate at lower temperatures, resulting in a change of the T.E.L.: ethylene bromide ratio in the fuel and an increase in lead oxide formation in the combustion chamber. It is therefore important to have a rapid method of determining the bromine content of aviation fuels before use, in addition to their lead content. To develop such a method is the aim of this work.

II - DETERMINATION OF THE BROMINE CONTENT OF ORGANIC COMPOUNDS.

If an organic compound contains carbon, hydrogen and bromine, e.g. ethylene bromide, the bromine must be converted before analysis into bromide ions. Thus in Carius' method the substance in question is generally oxidised by heating with fuming nitric acid in the presence of silver nitrate in a sealed tube and the bromine is determined as silver bromide. We shall deal below with the most important decomposition processes for organic bromine and with the quantitative bromine determination.

1. Conversion of organic bromine into bromide ions. Organic bromine can be converted into bromide not only by the generally applicable method of Carius but also by heating with halogen-free lime[3], giving calcium bromide.

Other halogen determinations, e.g. Parr's bomb[4], are based on the oxidation or decomposition of the organic compounds at high temperature in a sealed tube or flask, in the presence of calcium hydroxide [5] or sodium peroxide[6], [7]. Simple combustion with oxygen in the presence of sodium salts may also be used, giving sodium bromide.

A further possibility is hydrogenation at 350° to 400°C.[9] in a current of hydrogen at 400° to 450°C.[10] in presence of nickel and chromate. O. Tomicek and K. Petak[11] claim that quantitative saponification can be obtained with alcohol, caustic soda and zinc dust. Giacolone[12] treats organic bromine compounds with potassium dichromate and sulphuric acid, liberating bromine, which is led into aqueous hydrogen peroxide and then determined quantitatively. Rapid quantitative decomposition can also be achieved with hydrazine hydrate and active palladium - $N_2H_5OH \rightarrow N_2 + 2H_2 + H_2O$ - the resulting hydrogen is used catalytically to convert the organic bromine to bromide.

2. General methods for the determination of bromine. The above methods convert the organically combined bromine into ions; we shall now briefly describe the familiar volumetric and gravimetric methods of bromide estimation.

The gravimetric estimation consists of precipitation as silver bromide with silver nitrate in presence of nitric acid, filtering through porcelain filter crucible, drying at 110°C. and weighing.

E. Abrahaniczik and F. Blümel[14] developed a method, suggested by Emich and Schwarz-Bergkampf and based on Carius's work, in which Jena filter beakers are used for the filtration of the silver bromide. These have the advantage that they combine precipitation vessel and filter, avoiding volume variations, and reducing the time required for one estimation. An improved micro and semi-micro variation of Carius's method is described by R. H. Kimball and H. H. Wittenberg[16]. C. Tiedcke[17] also gives data on Carius's method. R. Berg and E. Becker[18] suggest using quinoline quinone (5.8) - (8) - hydroxy quinolyl - (5) - imide (5), (indoxin)- as a precipitation agent. Bromide is usually determined volumetrically by Volhard or Mohr's[19] method. The former consists of adding a considerable excess of N/10 silver nitrate solution, 5 cc. ferric-ammonium sulphate and sufficient dilute nitric acid to make the liquid colourless. The excess N/10 silver nitrate solution is back titrated with n/10 ammonium thiocyanate. Mohr's method entails titration of a neutral bromide solution containing a few drops of potassium chromate. Red silver chromate is precipitated only when the quantitative precipitation of the bromine ions is complete.

With strong oxidising agents in presence of hydrocyanic acid, bromides are converted in acid solution into cyanogen bromide.

$$Br^- + HCN = CNBr + H^+$$

Willard and Fenwick[20] use permanganate. According to Kurtnacker[21] the resulting cyanogen bromide can be titrated as follows :-

$$CNBr + 2S_2O_3^{--} + H^+ \rightarrow Br^- + HCN + S_4O_6^{--}$$

III - DETERMINATION OF THE BROMINE CONTENT OF AVIATION FUELS.

Compared with the determination of bromine in organic compounds, the new factor in the case of aviation fuels is that ethylene bromide is in solution in the fuel and at times only present in very small quantities. Moreover, it is not possible to separate the gasoline from ethylene bromide by distillation, as the boiling point of ethylene bromide (131°C.) coincides with that of the fuels.

On the basis of results published, some familiar methods were used for the bromine determination in gasoline.

1. Use of familiar bromine determination methods under various test conditions.

(a) Decomposition of ethylene bromide by oxidation: In the Berthelot-Mahler calorimeter bomb 1 gm. of gasoline was ignited by sparking a gelatine capsule in oxygen at 25 atm. pressure in presence of silver nitrate and slightly diluted nitric acid; the resulting silver bromide was determined by gravimetric and volumetric analysis. Although only about 3 gm. of oxygen were required for the burning of 1 gm. of gasoline and 6 gm. for the capsule, as against 40 gm. available in all, carbonisation occurred in the bomb. The bromine figures obtained were too low.

The bomb tests were continued, adding dilute caustic soda which is converted into sodium bromide. The sodium bromide was treated in nitric acid solution with excess silver nitrate and the resulting silver bromide determined by back titration with ammonium thiocyanate using ferric ammonium sulphate as indicator.

These tests were also unsatisfactory as the bromine figures were too low; and the results widely different, owing to the reaction of bromine with caustic soda, giving sodium bromide, and sodium hypobromite.

$$Br_2 + 2\ NaOH = NaBr + NaOBr + H_2O$$

Attempts were made to accelerate the oxidation with sodium peroxide, but this also gave no quantitative results.

Further tests were carried out in a combustion tube by the Grote-Krekeler method - 1 gm. of gasoline containing about 100 mgm. of ethylene bromide is burnt in a current of air and oxygen and the combustion gases containing free bromine are led into N/10 silver nitrate solution. The resulting silver bromide, determined either gravimetrically or volumetrically, was again much too low. The combustion gases containing free bromine were also led into N/10 K.I. solution, and the liberated iodine titrated with thiosulphate.

$$Br_2 + 2\,KI = I_2 + 2\,KBr$$

The bromine figures were still too low.

(b) Decomposition of ethylene bromide by hydrogenation: Attempts were made to reduce the organic bromine in the Grote-Krekeler apparatus with hydrogen in the presence of a catalyst. 1 gm. of the sample to be tested is converted to hydrogen bromide by reduction at 400°C. in a current of hydrogen in the presence of a nickel catalyst, and the resulting acid titrated with alkali. The reaction would be :-

$$(CH_2)_2\,Br_2 + 3\,H_2/Ni\text{-catalyst} = 2\,HBr + 2\,CH_4$$

Palladium was also used instead of nickel, but no HBr was obtained with either catalyst.

(c) Decomposition of ethylene bromide by saponification:

Extensive tests on the decomposition of ethylene bromide with alcohol, zinc and NaOH were instituted, on the basis of Tomicek and Petak's[11] work, who reported on Jansky's method for the determination of bromine. This involves saponification by refluxing 0.2 gm. of the substance with 25 c.c. of alcohol, 5 gm. NaOH and 0.5 gm. zinc dust. Gasoline containing 1% by weight of ethylene bromide was refluxed for various lengths of time, but all the results obtained were too low.

2. Decomposition of ethylene bromide with potassium ethylate in the bomb.

In the previous saponification tests with sodium, alcohol and Zu dust the temperature reached in the reflux condenser was insufficient for the quantitative decomposition of ethylene bromide. Recourse was therefore made to the bomb. Potassium was used instead of sodium, and it was not added to the fuel separate from the alcohol, but as potassium ethylate, which is more effective than sodium ethylate. Figure 1 shows the bomb with flask used for the test, and Figure 2 gives dimensions.

The fuel under test was put into a heat-resisting glass flask (Figure 1), and heated to various temperatures in the bomb. The box illustrated in Figure 3 is used to test four fuel samples at once. This arrangement allows very rapid continuous tests. The bomb was brought to various temperatures and after a given time, a bromide determination done on the reaction mixture, consisting of fuel, ethylene bromide and potassium ethylate :-

$$(CH_2)_2\,Br_2 + 2\,KOC_2H_5 \rightarrow 2\,KBr + (CH_2)_2 \begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}$$

The organic reaction product is unstable.

IV - TEST RESULTS ON BROMINE DETERMINATION IN THE BOMB.

From a large number of bromine determinations it emerged that particular attention must be given to make the bomb perfectly gas tight. It is therefore necessary to clean the seat of the cover after each determination, preferably with chloroform or acetone.

V - SUMMARY.

A method has been developed for the determination of the bromine content in aviation fuels; it makes rapid decomposition of ethylene bromide possible, using potassium ethylate in a bomb. The bromine is estimated volumetrically. An accurate test takes about 40 minutes, but for continuous tests this time can be considerably reduced.

VI - LITERATURE.

1. Szczepanski. Kraftstoff Vol.16 (1940) p.52.

2. O. Widmaier and L. Nenninger. Techn. Berichte der Z.W.B. Vol.9 (1942). p.111.

3. L. Gattermann. Die Praxis des organischen Chemikers, 22nd Edition. Verlag Walter de Gruyter and Co., Berlin and Leipzig, 1930.

4. Chao Lun Tseng, Mei Hu, Ming-Shin Chiang. J.Chin.Chem.Soc. Vol.3 (1935) p.39.

5. R.H.Kimball, Lewis L.Tufts, Ind.Eng.Chem. Analyt.Edition. Vol.10 (1938) p.530.

6. R. Kraus. Z. Analyt.Chemie Vol.117 (1939) p.243.

7. Eiji Ochiai, Kyosuke Tsuda, Syuusaka Sakamoto, J. Pharmc. Soc. Japan, Vol.57 (1937) p.301.

8. M. Jurecek, Chem. Zentralblatt 1936 I, p.1064.

9. A.Lacourt, C.R.Séances Acad.Sci. Vol.203 (1936) p.1367.

10. A.Lacourt, Mikrochemie. Vol.23 (1938), p.308.

11. O.Tomicek and K.Petak. Chem.Zentralblatt 1938 I, p.1838.

12. A.Giacalone. Ann.Chim.applicata. Vol.29 (1939) p.271.

13. M.Busch. Angew.Chemie Vol.38 (1925) p.519.

14. E.Abrahaniczik and F.Blümel. Mikrochim.Acta Vol.3 (1938) p.185.

15. Emich and Schwarz-Berkampf, Z.Analyt.Chem.Vol.69 (1926) p.336.

16. R.H.Kimball and H.H.Wittenberg. Ind.Eng.Chem.Analyt.Edition, Vol.9 (1937) p.48.

17. C.Tiedcke. Mikrochemie. Vol.23 (1938) p.301.

18. R.Berg and E.Becker. Z.Analyt.Chem.Vol.119 (1940), p.81.

19. Gattner and Birckenbach. Prakt.Anleitung zur Massanalyse, 3rd Edition. Verl. Conrad Wittwer, Stuttgart.

20. Willard and Fenwick, J.A.C.S. vol.45 (1923) p.45.

21. Kurtmacker. Zeitschr.anorg.Chem. Vol.116 (1921) p.243.

TABLE I.

Determination of the bromine content of fuels containing ethylene bromide

Description of fuel	Quantity of ethylene bromide in 50 cc. of fuel. mgms.	cc. of N/10 $AgNO_3$ used.	Results: Quantity of ethylene bromide in 50 cc. of fuel mgms.	% by wt.	Bromine content % by wt.
Louna Aviation	50	5.28	49.58	0.0992	0.0844
" "	50	5.26	49.39	0.0988	0.0840
" "	50	5.24	49.20	0.0984	0.0838
" "	25	2.64	24.79	0.0496	0.0422
" "	25	2.65	24.88	0.0497	0.0424
" "	25	2.64	24.79	0.0496	0.0422
Synthetic Gasoline	50	5.20	48.83	0.0977	0.0832
" "	50	5.19	48.73	0.0975	0.0830
" "	50	5.17	48.55	0.0971	0.0826
" "	25	2.64	24.79	0.0496	0.0422
" "	25	2.68	25.17	0.0503	0.0428
" "	25	2.67	25.07	0.0501	0.0426
Rumanian Gasoline	50	5.61	52.68	0.1054	0.0896
" "	50	5.37	50.42	0.1008	0.0858
" "	50	5.44	51.08	0.1022	0.0870
" "	25	2.88	27.04	0.0541	0.0460
" "	25	2.96	27.79	0.0556	0.0474
" "	25	2.91	27.33	0.0546	0.0465

TABLE 2.

Determination of bromine content of leaded fuels.

Description of fuel	T.E.L. content % by wt.	Calculated ethylene bromide content % by wt.	ccs.N/10 $AgNO_3$ used	Results: Quantity of ethylene bromide in 50 ccs. fuel. mgms.	Results: % by wt.	Bromine Content % by wt.
Rumanian Gasoline	0.1078	0.0626	3.26	30.61	0.0612	0.0521
" "	0.1078	0.0626	3.19	29.95	0.0599	0.0510
" "	0.0539	0.0313	1.78	16.71	0.0334	0.0284
" "	0.0539	0.0313	1.79	16.81	0.0336	0.0286
" "	0.2157	0.1253	6.48	60.85	0.1217	0.1036
" "	0.2157	0.1253	6.51	61.13	0.1223	0.1040
Leuna Gasoline	0.0539	0.0313	1.68	15.78	0.0316	0.0268
" "	0.0539	0.0313	1.70	15.96	0.0319	0.0272
" "	0.1078	0.0626	3.26	30.61	0.0612	0.0522
" "	0.1078	0.0626	3.19	29.95	0.0599	0.0510
" "	0.1659	0.0964	5.05	47.42	0.0948	0.0498
" "	0.1659	0.0964	5.05	47.42	0.0948	0.0808
" "	0.1659	0.0964	5.05	47.42	0.0948	0.0808
" "	0.1659	0.0964	5.07	47.61	0.0952	0.0810
Synthetic Gasoline	0.1659	0.0964	5.01	47.04	0.0941	0.0800
" "	0.1659	0.0964	5.08	47.7	0.0954	0.0812
" "	0.0830	0.0482	2.51	23.57	0.0471	0.0402
" "	0.0830	0.0482	2.48	23.29	0.0465	0.0396
" "	0.0830	0.0483	2.49	23.38	0.0468	0.0398
C3 fuel	0.2062	0.1198	6.10	57.28	0.1146	0.0974
" "	0.2062	0.1198	6.01	56.43	0.1129	0.0960
" "	0.2062	0.1198	5.92	55.59	0.1112	0.0946
B4 fuel	0.2011	0.1168	6.10	57.28	0.1146	0.0974
" "	0.2017	0.1172	6.10	57.28	0.1146	0.0974
" "	0.2017	0.1172	6.07	57.00	0.1140	0.0970
" "	0.2031	0.1180	6.01	56.43	0.1129	0.0960
" "	0.2062	0.1198	6.01	56.43	0.1129	0.0960

List of Illustrations