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OXYGEN FLASK METHOD FOR DETERMINING ELEMENTS IN OILS – AN EVALUATION

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The oxygen flask, combustion technique for determining phosphorus, sulfur, and chlorine in oils was evaluated using military lubrication oils as representative material. The concentration of those elements, after combustion of the samples, was determined spectrophotometrically. This technique is a rapid, simple, and inexpensive method for performing nonroutine analyses.

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OXYGEN FLASK METHOD FOR DETERMINING ELEMENTS IN OIL – AN EVALUATION

I. INTRODUCTION

1. **Background.** Military Laboratories are only equipped with apparatus suitable for performing quality surveillance tests of the supplied lubrication products according to military specifications.[1] These surveillance tests include the determinations of concentration of phosphorus, sulfur, and chlorine in individual lots. The military lubrication oils were selected for this study as representative products containing these elements. In addition, MERADCOM is engaged in research on these oils because it has the custodial responsibility for military automotive engine and gear-lubricating oils.[2]

The conformance tests for determination of these elements specify ASTM methods.[3] These methods are reliable for routine analyses; however, they are often tedious and time-consuming and require special complex equipment which may be bulky and expensive. Military Laboratories need a rapid, simple, and inexpensive method for nonroutine determination of phosphorus, sulfur, and chlorine. Such a method could be incorporated into military specifications for lubricating oils.[4] Ideally, this method should utilize readily available, portable, and unencumbering equipment.

The oxygen flask, combustion technique, originally developed by Schoniger,[5] appeared promising for such applications.[6] The combustion technique

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[1] Military Specifications:
MIL-HDBK-200D, *Military Standardization Handbook*, "Quality Surveillance Handbook for Fuels, Lubricants, and Related Products," 1 March 1971.
MIL-L-50096A, *Laboratory, Petroleum, Base*, 30 Dec 1963.
MIL-L-51050A(GL), *Laboratory, Petroleum, Semitrailer Mounted*, 13 Dec 1965.

[2] Military Sepcifications:
MIL-L-2104C, *Lubricating Oil, Internal Combustion Engine, Tactical Service*, 20 Nov 1970.
MIL-L-46152, *Lubricating Oil, Internal Combustion Engine, Administrative Service*, 20 Nov 1970.
MIL-L-2105B, *Lubricating Oil, Gear, Multipurpose*, 19 Feb 1962.

[3] *Annual Book of ASTM Standards*, American Society for Testing and Materials, Part 23, Philadelphia, PA (1975):
D1091-64, "Phosphorus in Lubricating Oils and Additives."
D129-64, "Sulfur in Petroleum Products (General Bomb Method)."
D1552-64, "Sulfur in Petroleum Products (High Temperature Method)."
D808-63, "Chlorine in New and Used Petroleum Products (Bomb Method)."
D1317-64, "Chlorine in New and Used Petroleum Products (Sodium Alcoholate Method)."

[4] Military Specifications:
MIL-L-2104C, *Lubricating Oil, Internal Combustion Engine, Tactical Service*, 20 Nov 1970.
MIL-L-46152, *Lubricating Oil, Internal Combustion Engine, Administrative Service*, 20 Nov 1970.
MIL-L-2105B, *Lubricating Oil, Gear, Multipurpose*, 19 Feb 1962.

[5] W. Schöniger, Mikrochim Acta, *1955*, 123; *1956*, 867.

[6] C. Liddell, J. Inst. Petrol., *48*, 221 (1962).

consists of burning the sample, absorbed on a filter paper placed in a platinum gauze basket, in a glass flask filled with oxygen at atmospheric pressure and containing a suitable liquid absorbent. Combustion takes about 30 seconds. The elements present are then determined by suitable procedures. This technique was evaluated for determining phosphorus, sulfur, and chlorine content in oils using engine and gear-lubricating oils as representative materials. This report describes the results of the development and evaluation effort. The atomic absorption measurements were performed at MERADCOM by Mr. George Oswald.

II. RESULTS AND DISCUSSION

2. **Determination of Phosphorus.** Engine and gear-lubricating oils commonly contain organophosphorus-sulfur compounds and their derivatives as antioxidants, corrosion inhibitors, antiwear agents, and dispersant-detergents.[7] In this study, the oxygen-combustion analysis for phosphorus was developed by modifying the Schöniger method[8] [9] [10] [11] and combining it with an ASTM spectroscopic procedure.[12] In this analysis, the sample is burned in the presence of sodium carbonate, and the combustion products containing sodium phosphate are absorbed in sulfuric acid. The phosphoric acid formed is then treated with an ammonium molybdate-hydrazine mixture to give the molybdenum blue complex. The absorbance of this colored compound, measured at 820 nm, is proportional to the concentration of phosphorus. The results of determination of phosphorus in oils are presented in Table I (tests 105, 106, 108, 109, and 110). The repeatability lies within the values recommended by the standard phosphorus oxidation method, ASTM D1091.[13] Also, the deviation of the mean from the value obtained by the ASTM method is small. Other elements, usually present in most lubricating oils, did not interfere in this procedure. The capsule, employed in other methods as a sample carrier,[14] [15] was not used here. It was found that the capsule material, gelatine and cellulose acetate, contained phosphorus and, therefore, would distort the results (Table I, test 115).

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[7] M. Kolobielski, *Determination of Zinc Dialkyl (Diaryl) Dithiophosphate in Lubricating Oil*, AD757605, Feb 1973.

[8] K. D. Fleischer, *et al.*, Anal. Chem., 30, 152 (1958).

[9] J. E. Barney II, *et al.*, Anal. Chem., 31, 1394 (1959).

[10] S. J. Gedansky, *et al.*, Anal. Chem., 32, 1447 (1960).

[11] "Proposed Methods for Petroleum and Petroleum Products," Appendix IV, American Society for Testing and Materials, Philadelphia, PA, 1965.

[12] "Annual Book of ASTM Standards," American Society for Testing and Materials, Part 25, Philadelphia, PA, Test D3231, 1975.

[13] "Annual Book of ASTM Standards," American Society for Testing and Materials, Part 23, Philadelphia, PA, Test D1091-64, 1975.

[14] S. J. Gedansky, *et al.*, Anal. Chem., 32, 1447 (1960).

[15] "Proposed Methods for Petroleum and Petroleum Products," Appendix IV, American Society for Testing and Materials, Philadelphia, PA, 1965.

Table 1. Determination of Phosphorus

			% Phosphorus		
Test No.	Material	Elements Present	By ASTM D1091	By Proposed Method	
					Mean
105	Engine Oil: MIL-L-45199B	P,S,Ca,Ba,Zn, C,H,O,N	0.052	0.060	0.061
106	"	"	"	0.059	
108	"	"	"	0.064	
109	Gear Oil: MIL-L-2105B	P,S,Cl,C,H,O	0.060	0.058 0.062	0.060
110	"	"	0.110	0.112 0.110	0.111
115	Gelatine Capsule Cellulose Acetate	P,C,H,O "	–	0.013 0.071	

3. **Determination of Sulfur.** Several methods employing the oxygen-combustion technique have been reported. All these methods have a similar combustion procedure for sulfur, present in the organic compound, as the first stage. The first stage results in the formation of sulfuric acid. These methods differ only in the way of determining the sulfuric acid. The simplest method, employed by many authors, involves a variety of titrimetric procedures: with sodium hydroxide in the presence of methyl red,[16] [17] [18] [19] with standard barium chloride solution in the presence of Sulfonazo III indicator,[20] or with barium perchlorate in the presence of Thorin[21] [22] and Arsenazo III indicators.[23]

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[16] I. Lysy and J. E. Zarembo, Anal. Chem., 30, 428 (1958).

[17] C. Liddell, J. Inst. Petrol., 48, 221 (1962).

[18] N. H. Furman, *Standard Methods of Chemical Analysis,* D. Van Nostrand, Co., Inc., New York, N.Y., p. 1014 (1966).

[19] A. R. Crawford and G. V. Dyroff, "An Evaluation of Methods for Determining Sulfur in Fuel Oils," Air Pollution Control Association 63rd Annual Meeting, Paper 70-46 (June 1970).

[20] "Annual Book of ASTM Standards," American Society for Testing and Materials, Part 30, Philadelphia, PA, Test E443-74 (1975).

[21] D. B. Ratcliffe and A. T. S. Cunningham, Fuel, 47, 89 (1968).

[22] L. H. Scroggins, J. Assoc. Official Anal. Chem., 56, 892 (1973).

[23] S. M. Ahmed and B. J. P. Whalley, Fuel, 48, 217 (1969); 51, 190 (1972).

A spectroscopic method has also been suggested.[24] [25] It consists of reacting the sulfuric acid with barium chloranilate in a buffered solution of pH 4.3 and then determining the liberated chloranilic acid by measuring its absorbance at 330 nm. In another spectroscopic method, the sulfuric acid formed is reacted with a known amount of barium chloride solution, and the excess of barium is determined by atomic absorption spectroscopy.[26] Still another method suggests reacting the sulfuric acid with a known and excessive amount of barium bromate to produce a precipitate of barium sulfate. The excess of barium bromate is determined iodometrically.[27]

The first three methods were investigated in this study. The results are presented in Table 2. The titrimetric method was tested on a sulfur standard containing an organosulfur compound in a hydrocarbon oil (tests 176, 176a, and 177) and on a formulated lubricating oil containing phosphorus, calcium, barium, and zinc in addition to carbon, hydrogen, oxygen, sulfur, and nitrogen. The titration of the product, obtained upon combustion of the sulfur standard, gave values close to those expected. However, the results from the lubricating oil were too high because of formation of phosphoric, in addition to sulfuric, acid during the combustion and oxidation reaction.

The spectroscopic method with barium chloranilate was applied to a sulfur standard solution (test 10), engine oils (test 11), and gear oils (test 12). The duplicate values in each test were close, and the deviation of the mean from the expected value was also small in tests 10 and 11. In the case of gear oil (test 12), the deviation was too high. It was not established if the error lay in this method or was due to a mistaken value reported by the laboratory which performed the standard determination of sulfur by the bomb method (ASTM D129).[28]

In the method where barium excess was determined by atomic absorption spectroscopy, the measurements were done at 455 and 554 nm. In the case with the higher wavelength, potassium acetate was added to the solution to suppress the ionization of barium. The duplicate results and the means are close to the values given for the standard solutions (tests 26, 22, and 21) or determined by other methods (tests 17, 27, 28, and 17a). In both spectroscopic methods (with barium chloranilate and atomic absorbtion spectroscopy, no interference by metals or phosphorus was observed.

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[24] R. J. Bertolacini and J. E. Barney II, Anal. Chem., 29, 281 (1957).

[25] R. W. Klipp and J. E. Barney II, Anal. Chem., 31, 596 (1959).

[26] H. W. Lautenbacher and H. W. Baker, Amer. Laboratory, 4, No. 8, 45 (1972).

[27] Y. A. Gawargious and A. B. Farag, Talanta, 19, 641 (1972).

[28] "Annual Book of ASTM Standards," American Society for Testing and Materials, Part 23, Philadelphia, PA, Test D129-64, 1975.

Table 2. Determination of Sulfur

Test No.	Material	Elements Present	% S By Other Method	Procedure of Proposed Method	% S By Proposed Method	
						Mean
176	Standard	S,C,H	1.0305	Titrimetric	0.9984	
177	"	"	"	"	0.8030 0.9024	0.9013
176a	"	"	0.9893	"	0.786 0.887 0.873	0.849
175	Engine Oil: MIL-L-45199B	S,P,Ca, Ba,Zn,C,H,O,N	0.390 (ASTM D129)	"	0.510	
10	Standard	S,C,H,	0.1989	Barium Chloranilate	0.1575 0.1864	0.1720
11	Engine Oil	as in 175	0.390 (ASTM D129)	"	0.4137 0.3783	0.3960
12	Gear Oil: MIL-L-2105B	S,P,Cl, C,H,O	0.370 (ASTM D129)	"	0.2295 0.2741	0.2518
26	Standard	S,C,H	0.1989	AAS,* at 554 nm	0.165 0.217	0.1910
22	"	"	0.9893	"	0.973 1.047	1.0100
17	Engine Oil	as in 175	0.39	"	0.29 0.35	0.32
27	"	S,P,Ca,Ba,Zn,C, H,O,N	0.46 (ASTM D129)	"	0.442 0.421	0.432
28	"	"	0.27 (ASTM D129)	"	0.197 0.232	0.215
21	Standard	S,C,H,O	0.9893	AAS, at 455 nm	0.951 0.904	0.928
17a	Engine Oil	as in 175	0.39	"	0.38 0.41	0.395

* Atomic Absorption Spectroscopy.

4. **Determination of Chlorine.** Several methods were reported for the determination of chlorine by the oxygen flask technique. One simple method involves reaction of the chloride, formed upon combustion, with mercuric chloranilate in 0.05 N nitric acid and determination of the absorbance of the liberated chloranilic acid at 306 nm.[29] The chloride can also be determine by amperometric,[30] or potentiometric titration with silver nitrate solution,[31] [32] [33] atomic absorption,[34] complexinmetric

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[29] J. E. Barney II and R. J. Bertolacini, Anal. Chem., 29, 1187 (1957); 30, 202 (1958).

[30] D. B. Ratcliffe and T. L. Young, Fuel, 47, 185 (1968).

[31] "Annual Book of ASTM Standards," American Society for Testing and Materials, Part 30, Philadelphia, PA, Test E-442 (1975).

[32] M. Corner, Analyst, 84, 41 (1959).

[33] J. Haslam, *et al.*, Analyst, 85, 556 (1960).

[34] E. D. Truscott, Anal. Chem., 42, 1657 (1970).

titration,[35] or titration with mercuric nitrate.[36]

The spectroscopic method, with mercuric chloranilate, was employed here for chlorine determination of a chlorine standard, a gear oil, and an oil additive (Table 3). The standard chlorine solution was analyzed in duplicate, and the analyses were replicated on different days (tests 187, 188, and 189). Samples of a gear oil (tests 185 and 191) and an oil additive (test 3) were also analyzed under the same conditions. All these results indicate that the repeatability of this method is good and its value lies within the repeatability value (0.07% for materials with 0.1 to 2% chlorine content) recommended by another method involving a bomb oxidation technique.[37] In these tests, the deviation of the mean values from the corresponding values determined by other methods and other laboratories was relatively small. Since it was reported that metals interfere in this spectroscopic method,[38] a test was performed in which the cations were removed from the combustion product by treatment with an ion exchange resin (test 2). The mean chlorine content was much closer to the expected value than the chlorine content obtained in tests without the treatment (tests 185 and 191).

Table 3. Determination of Chlorine

Test No.	Material	Elements Present	% CL By Other Method	Procedure of Proposed Method	% CL By Proposed Method	
						Mean
187	Standard	Cl,C,H	0.899	Regular	0.847 0.771	0.809
188	"	"	"	"	0.698 0.781	0.740
189	"	"	"	"	0.890 0.851	0.870
185	Gear Oil: MIL-L-2105B	Cl,S,C,H,O	1.49 (ASTM D808)	"	1.09 1.07	1.08
191	"	"	"	"	1.12 1.18	1.15
3	Standard prepared from extreme pressure gear oil additive	Cl,S,C,H,O	0.6037 (ASTM D808)	"	0.692 0.623	0.657
2	Gear Oil	as in 185	1.49	with ion exchange resin	1.23 1.25	1.24

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[35] J. Z. Faleon, *et al.*, Anal. Chem., 47, 171 (1975).

[36] N. P. Sosnina and T. N. Krasnova, Khimiia I. Tekhnologiia Topliv I. Masel, 17, 49 (1972).

[37] "Annual Book of ASTM Standards," American Society for Testing and Materials, Part 23, Philadelphia, PA, Test D808-63 (1975).

[38] J. E. Barney II and R. J. Bertolaeini, Anal. Chem., 29, 1187 (1957); 30, 202 (1958).

III. EXPERIMENTS

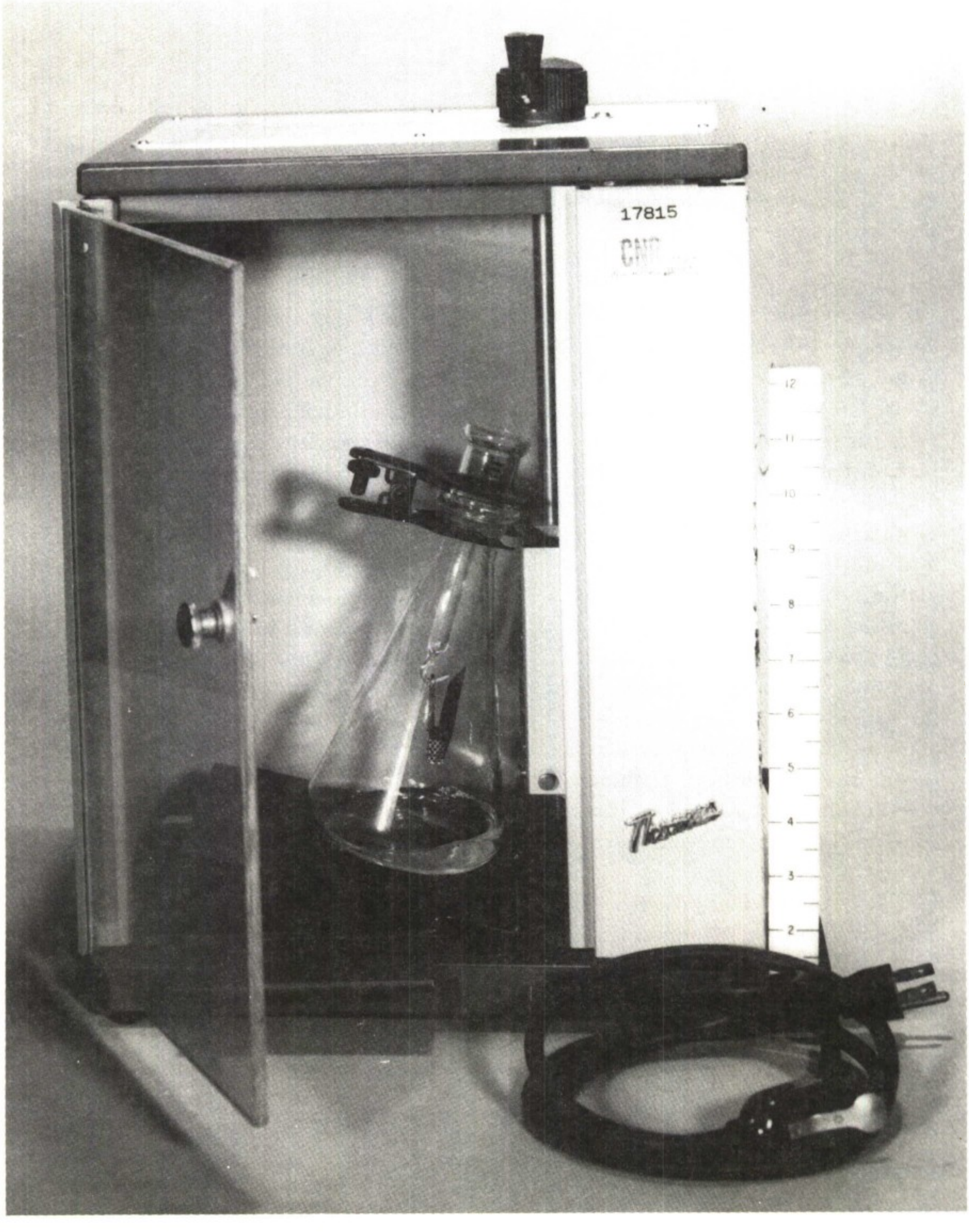
5. **Apparatus.** The apparatus is shown in the figure (page 8). The main parts are: 500- to 1000-ml conical flask of borosilicate glass with a spherical joint and a flaring lip; glass stopper with a hook and a spherical ground joint; platinum gauze basket as a sample carrier; pinch clamp; safety metal cabinet with transparent plastic door and inclined platform for the flask; and infrared light igniter with a cord and a line switch for remote firing.

6. **General Combustion Procedure.** The black paper sample wrapper (sample area 32 by 30 mm, with "fuse" 8 by 38 mm) is folded to form a cup and then placed in the platinum carrier with the "fuse" projecting. The sample carrier with the paper is tared, and the sample (10 to 50 mgs) is introduced into the paper cup. The platinum carrier is suspended on the hook of the stopper, and the latter is set aside. The combustion flask is first charged with a suitable absorbent and then filled, for about 3 to 4 minutes, with oxygen which is passed in through a delivery tube reaching nearly to the bottom of the flask. The stopper with the sample in the platinum carrier is inserted into the flask and secured with the pinch clamp. The flask is placed on the inclined platform inside the metal cabinet. The flask is positioned within the chamber by adjusting the crank handle and the platform so that the focal point of the lamp beam (1.5 inches in front of the red filter) is on the black paper "fuse." The remote firing is performed by means of the line switch which is located 4 feet from the cabinet. After the combustion is complete, the flask is allowed to cool for about 1 minute, then the platinum basket is dropped into the absorbent, and the flask is well shaken in order to absorb the combustion products. Further procedures vary with particular element determination. A procedure blank is run simultaneously with each sample. The blank consists of reagents to which no unknown sample is added.

7. **Safety Precautions.** Many combustions have been carried out without mishap. However, the following precautions should be exercised. The combustion flask must not contain any residue or vapors of organic solvents which may produce a violent explosion upon ignition. The combustion must be carried out in a hood in the safety cabinet. The operator should wear goggles, face shield, and gloves for protection during the combustion operation.

8. Determination of Phosphorus.

a. **Procedure.** The unknown oil sample is weighed on to 0.03 g of sodium carbonate in the black paper wrapper cup prior to combustion and then covered with an additional 0.02 g of Na_2CO_3. The absorbent used, 10 percent sulfuric acid, is



Combustion Assembly

placed in the combustion flask. After the combustion is completed, the flask is intermittently shaken, and then the stopper is washed down with distilled water. A freshly prepared 50 ml of molybdate-hydrazine reagent is added, and the mixture is transferred to a 100-ml volumetric flask. The combustion flask is rinsed with water, the washings are added to the volumetric flask, and the solution is diluted to 100 ml with water and mixed well. After the solution is mixed, the stopper is removed, and the flask is placed in a water bath (71 to 99° C) for 25 minutes. The flask is then cooled to room temperature, and the absorbance of the blue-colored complex is measured at 820 nm in a 1-cm cell using distilled water in the reference cell. The absorbance of the unknown sample solution is corrected by subtracting the absorbance of the blank. The concentration of phosphorus is determined by comparing the corrected absorbance of the unknown sample with the calibration curve.

b. **Molybdate-Hydrazine Reagent.** A 20-g sample of ammonium molybdate tetrahydrate ($(NH_4)_6MO_7O_{24} \cdot 4H_2O$) is dissolved in a solution of concentrated sulfuric acid (225 ml) in water (500 ml). Next, the solution is transferred to a 1000-ml flask and diluted to the mark with water. In another 1000-ml flask, hydrazine sulfate ($H_2NNH_2 \cdot H_2SO_4$, 1.5g) is dissolved in 1ℓ of water. The reagent is prepared by mixing 25 ml of ammonium molybdate solution with 10 ml of hydrazine sulfate solution in a 100-ml volumetric flask and diluting to the mark with water. The reagent is unstable and should be used within 4 hours.

c. **Calibration Curve.** A 4.3930-g sample of dry potassium dihydrogen phosphate (KH_2PO_4) is dissolved in 150 ml of 10% sulfuric acid in a 1000-ml flask and diluted to the mark with water. A 10-ml sample of this solution is then diluted with water to 1000-ml volume to give a standard phosphorus solution of 10.0 μg phosphorus per ml. Exact amounts of the standard solution (0, 1.0, 2.0, 3.0, and 4.0 ml) are transferred into 100-ml volumetric flasks. This is followed by addition of 10 ml of 10% sulfuric acid, 50 ml of molybdate-hydrazine reagent, and then water to the 100-ml mark. These phosphorus solutions are submitted to the same sequence of operations as the unknown sample – heating, cooling, and measuring the absorbance. The calibration curve is obtained by subtracting from each absorbance the absorbance of the 0-ml phosphorus standard and plotting these corrected absorbances against the concentration of phosphorus in each standard solution (in μg per ml).

9. Determination of Sulfur.

a. **Titrimetric Procedure.** The oil sample (0.02 to 0.05 g) is weighed directly on to the black paper folded wrapper. The flask is charged with 10 ml of 3% hydrogen peroxide solution. After combustion, the solution is boiled gently to remove carbon dioxide and to destroy hydrogen peroxide. Then, it is cooled and titrated with 0.02 N sodium hydroxide solution in the presence of methyl red indicator. The volume of the titrant used in the blank titration is subtracted from that of the unknown sample.

b. **Spectroscopic Procedure with Barium Chloranilate.** The weighing and combustion stages are similar to those described above. After combustion and heating, the flask content is transferred to a 100-ml volumetric flask. Ethanol (95%, 50 ml) is then added, followed by 10 ml of the buffer solution, water to the mark, and 0.3 g of solid barium chloranilate. The volumetric flask is shaken for 15 minutes, and then the content is filtered through Whatman No. 42 filter paper to remove the excess of barium reagent. The absorbance of the filtrate is measured at 330 nm in a 1-cm cell against the reagent blank (50% of 95% C_2H_5OH + 10% of buffer solution + 40% of water) in the reference cell. This absorbance is corrected by subtracting from the measured value the absorbance of the blank. The concentration of sulfur is determined by comparing the corrected absorbance of the unknown sample with the calibration curve.

The buffer (pH 4.3) required in the reaction is an aqueous solution of 0.02 M concentration of both acetic acid and sodium acetate. To obtain the calibration curve, a 2.06057-g sample of anhydrous ammonium sulfate is dissolved in 100 ml of water. A 10-ml sample of this solution is then diluted with water to 1000-ml volume to give a standard sulfur solution of 5 μg of sulfur per ml. Exact amounts of the standard solution (5, 10, 15, 20, 25, and 30 ml) are added separately to 100-ml volumetric flasks. This is followed by addition to each flask of the following materials: 10 ml of buffer solution, 50 ml of 95% ethanol, water up to the 100-ml mark, and 0.3 g of barium chloranilate. These sulfur solutions are submitted to the same sequence of operations as the unknown sample – shaking, filtering, and measuring the absorbance against the reagent blank in the reference cell. Finally, the absorbance is plotted against the sulfur concentration to give the calibration curve.

c. **Spectroscopic Procedure with Barium Chloride.** The oil sample (20 to 50 mg) is weighed on to the folded black wrapper which is then wetted with two drops of water to reduce the combustion rate and to minimize soot formation. The combustion flask contains 20 ml of barium chloride solution of known concentration (for example, 50 ppm Ba) and a few drops of 30% hydrogen peroxide. After combustion, the flask is shaken and then allowed to stand for 20 minutes. It is again shaken, and the solution is transferred to a 7-dram glass vial. The vial is cooled in an ice-bath and centrifuged at 1500 rpm for 30 minutes. The supernatant fluid is aspirated into the atomic absorption spectrophotometer without disturbing the centrifugate. The absorbance of the solution is measured at 455 nm or 554 nm. In the latter case, potassium acetate (0.25 g CH_3COOK per 100 ml) is added to the combustion flask. The sulfur content is calculated from the formula:

$$\% S = \frac{(\text{ppm Ba used} - \text{ppm Ba blank}) \times 20 \times 0.02335}{\text{weight of sample, in mg}}$$

(using 20-ml volume of a standard barium solution).

The standard barium solutions (10, 20, 40, 50, 75, 100, 250 ppm Ba) are prepared by dissolving an 0.8895-g sample of $BaCl_2 . 2H_2O$ in 500 ml water and then taking measured volumes of this stock solution and diluting them with water to exact volumes in volumetric flasks. The "ppm Ba used" is the difference between the barium concentration of the standard barium chloride solution (in the 20-ml sample) and the concentration in the supernatant fluid, after the reaction, as determined by the atomic absorption spectrophotometry.

10. **Determination of Chlorine.** The oil sample (10 to 50 mg) is weighed on to the folded black paper. The combustion flask contains 5 ml of 0.1 N sodium hydroxide solution and 5 ml of 3% hydrogen peroxide. After the combustion is completed, the solution is boiled for a few minutes on a hot plate and then cooled. The content is transferred to a 100-ml volumetric flask and treated with 5 ml of 1 N nitric acid and 50 ml of Methyl Cellosolve and completed with water to the mark. Mercuric chloranilate (0.2 g) is then added, the flask is shaken for 15 minutes, and the excess of the mercuric reagent is removed by filtration through Whatman No. 42 filter paper. The absorbance of the filtrate is measured at 306 nm in a 1-cm cell against a reagent blank in the reference cell (filtrate from: 5 ml 1 N HNO_3, 50 ml Methyl Cellosolve, 45 ml water, and 0.2 g mercuric chloranilate). The absorbance is corrected by subtracting from the measured value the absorbance of the blank. The chloride concentration is then obtained by comparing the corrected absorbance with the calibration curve prepared from standard ammonium chloride solution. In those cases when interfering cations (Ba,Ca,Pb,Zn) are present in the unknown sample, they are removed by using the ion exchange resin, Amberlite IR-120, hydrogen form. The regular procedure is modified by adding 0.5 g of this resin to the combustion flask after the combustion is completed. The mixture is filtered through S and S No. 589 filter paper, and the filtrate is transferred to a 100-ml flask. Further operation sequence follows the regular procedure.

The standard ammonium chloride solutions (0.04-, 0.10-, 0.20-, 0.40-, and 0.60-mg chloride per 100 ml) are made by diluting the standard stock solution (1.5105 g of ammonium chloride in 1000 ml water). A sample of each standard solution of known concentration is treated the same way as the known chlorine-containing material. The sample is admixed with 5 ml 1 N HNO_3, 50 ml Methyl Cellosolve, completed with water to the 100-ml mark, and then treated with 0.2 g of mercuric chloranilate in a 100-ml flask. After filtration, the absorbance of each filtrate is measured at

306 nm, and the values are plotted against the chloride concentration to give the calibration curve.

IV. CONCLUSIONS

11. Conclusions. This study was concerned, mainly, with the evaluation of the oxygen-combustion method as a novel technique for potential use by the Military Laboratories. Specifically, this technique was considered for potential inclusion in military specifications for automotive lubricating oils. The short duration of this study did not generate sufficient data for performing a statistical analysis to determine the precision of these analytical methods. However, it is apparent that the oxygen flask, combustion method is a rapid, simple, and inexpensive laboratory technique for determining such elements as phosphorus, sulfur, and chlorine present in military oils and related products.

Among the different procedures tested on the samples containing sulfur and chlorine, the methods which involve barium chloranilate for sulfur and mercury chloranilate with ion exchange resin for chlorine appear to be the most reliable.

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