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LIVERMORE

THE ANALYSIS OF BIS(2,2-DINITRO-2-FLUOROETHYL) FORMAL (FEFO) IN LX-09-0

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THE ANALYSIS OF BIS (2, 2-DINITRO-2-FLUOROETHYL) FORMAL (FEFO) IN LX-09-0

ABSTRACT

A method for the analysis of bis (2, 2-dinitro-2-fluoroethyl) formal (FEFO) in the explosive LX-09-0 is discussed in this publication. After combustion in an oxygen bomb, fluoride is titrated potentiometrically with standard lanthanum(III) solution. A fluoride ion indicating electrode and a calomel reference electrode are used in conjunction with an expanded-scale pH meter.

INTRODUCTION

The explosive LX-09-0 has the approximate composition:

(1)	1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazacyclooctane (HMX)	93 percent
(2)	Poly(2, 2-dinitropropylacrylate)(DNPA)	5 percent
(3)	Bis(2, 2-dinitro-2-fluoroethyl) formal (FEFO)	2 percent

Procedures for the analysis of this explosive have been reported previously.[1] FEFO is usually analyzed by combustion of the explosive in an oxygen bomb, followed by titration of the resulting fluoride with thorium nitrate in the presence of methylthymol blue indicator.[2] However, since operators have reported difficulties in perceiving the endpoint of this titration, we have used a fluoride ion specific electrode as the indicating electrode in the potentiometric titration of fluoride with lanthanum (III). The method discussed here may also be used for the determination of fluoride in inorganic and organic materials after removal of interfering ions.

EXPERIMENTAL

Equipment

(1) Parr No. 1105C self-sealing oxygen bomb, 340 ml capacity, and accessories previously described[1]

(2) pH meter, Corning Model 12, or similar model capable of scale expansion

(3) Fluoride ion electrode, Orion Model 94-09

(4) Calomel reference electrode, sleeve type, double junction, Orion model 90-01

(5) Buret, graduated in 0.05 ml divisions.

Reagents

(1) Sodium Fluoride, reagent grade.

(2) Lanthanum nitrate solution, 0.02M. (Dissolve 8.66 g of the hexahydrate in 1 liter of distilled water.)

Procedure

Standardization of Reagent. Prepare a standard fluoride solution containing approximately 0.3 mg fluoride per ml (663 mg of sodium fluoride per liter). Use this solution to standardize the lanthanum (III) solution as follows: Deliver 10.00 ml aliquots into plastic beakers containing a plastic-coated stirring bar. Dilute to about 50 ml with water. Adjust the pH to between 5 and 7 with 0.1N hydrochloric acid and sodium hydroxide, using a pH meter. Titrate potentiometrically with 0.02M lanthanum (III) solution 50 ml with water. Adjust the pH to between 5 and 7 with 0.1N lanthanum (III) solution by means of an expanded scale pH meter provided with a fluoride specific ion indicating electrode and a calomel reference electrode. As the endpoint is approached (as indicated by the increasing potential jumps) add the titrant in 0.1 ml increments. Determine the equivalence point from a titration curve or by calculation.[3]

Analysis

Prepare and combust the sample as described previously.[1] Transfer the bomb contents quantitatively to a plastic beaker (150 to 250 ml capacity). Adjust the pH to 4.4 with hydrochloric acid, using a pH meter. Bring the contents to boil on a hotplate to expel the carbon dioxide generated during combustion. Then cool the solution to room temperature. Adjust the pH to between 5 and 7, and titrate with lanthanum (III) as described above (Standardization of Reagent). 1 mg fluoride corresponds to 8.4246 mg FEFO. Standardize the titrant with an amount of fluoride similar to that expected in the analyzed sample to achieve best results.

RESULTS AND DISCUSSION

The fluoride ion specific electrode is a relatively new tool which has attracted the attention of several authors.[4-15] The experiments discussed here were undertaken to provide an alternate method for the analysis of FEFO in the explosive LX-09-0. The analytical method is largely based on the work of Lingane,[4,12] who investigated several titrants for fluoride. He recommended lanthanum (III) because it yields the largest rate of change of potential at the equivalence point and the maximum rate of potential change is closer to the equivalence point than with thorium (IV).[4] In a later paper Lingane suggests the use of 60 percent ethanol as the titration medium to further improve the titration curve.[12] The effect of an increasingly alcoholic titration medium is demonstrated in Figure 1. In 80 percent alcohol somewhat unsteady potentials were obtained, possibly due to the evaporation of the solvent; hence this high a proportion of alcohol is not recommended.

Light and Mannion[15] recently described a modified Schöniger combustion for the analysis of fluorine in organic compounds. The authors used thorium (IV) titrant in 80 percent ethanol which, of course, requires temperature control to obviate changes in the normality of the titrant. The fairly acidic medium (0.01M nitric acid) recommended decreases the sensitivity of the titration although, according to their findings, it reduces the hydrolysis of the titrant. This hydrolysis is less pronounced with

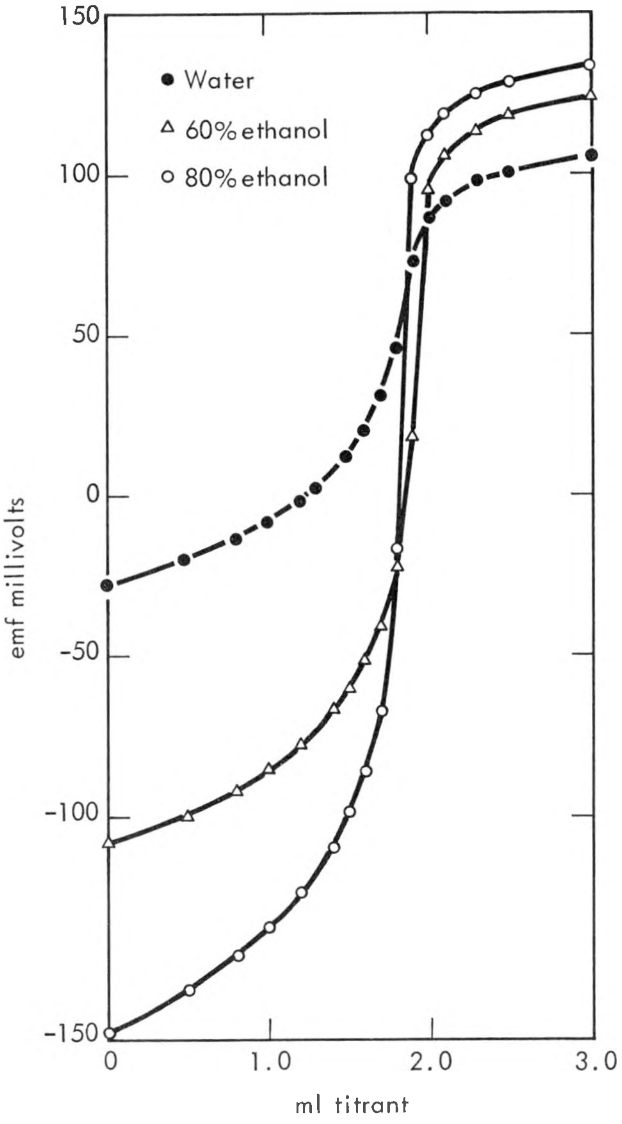

Fig. 1. Titration of 2.28 mg fluoride with 0.02M La (III).

lanthanum (III) than with thorium (IV). Their acidic medium in combination with the small sample size in the Schöniger combustion seem to eliminate the interference from carbon dioxide. However, combustion of 1 g in the oxygen bomb generates large amounts of carbon dioxide which interfere in the fluoride determination by the precipitation of lanthanum carbonate. This interference is eliminated by boiling after acidification to pH 4.4.[16]

In our experiments titration endpoints were calculated,[3] although they can be obtained from titration curves. Under experimental conditions the recovery of fluoride depended somewhat on the amount of fluoride present as shown in Table I and, graphically, in Fig. 2. We therefore standardized the titrant against an amount of fluoride close to that expected in the unknown samples. This relationship may possibly be due to the slight solubility of lanthanum fluoride in water and can perhaps be reduced by a partially non-aqueous medium. Also, better recoveries over a wider range may possibly be obtained by titration to a potential which is the point of maximum inflection as predetermined by titration of a standard under identical experimental conditions.[4,15]

It is advisable to insulate the titration vessel from the magnetic stirrer since the electrode behavior depends on the Nernst factor, $\frac{2.3RT}{F}$, where T is the absolute temperature in °K. It should be noted that an error of 0.1 mV in reading the potential for a monovalent ion such as fluoride will produce an error of 0.4 percent of that ion.

The results for the analysis of FEFO[17] in a sample of LX-09-0 are presented in Table II. Although the standard deviation by the potentiometric method (0.3) compares favorably with that obtained by the methylthymol blue method (0.06), it is noteworthy that the latter results were obtained from three installations by four operators. The average by the potentiometric method was 0.06 percent lower than by the methylthymol blue method, but this is within the ±3 percent absolute accuracy expected according to the manufacturer of the electrode.

Interferences can be expected from polyvalent cations, such as Si^{+4}, Al^{+++}, and Fe^{+++}, which complex the fluoride ion. Sulfate and phosphate may also interfere[15], but can be separated by ion exchange[18,19] or by distillation of the fluorine as fluosilicic acid[20].

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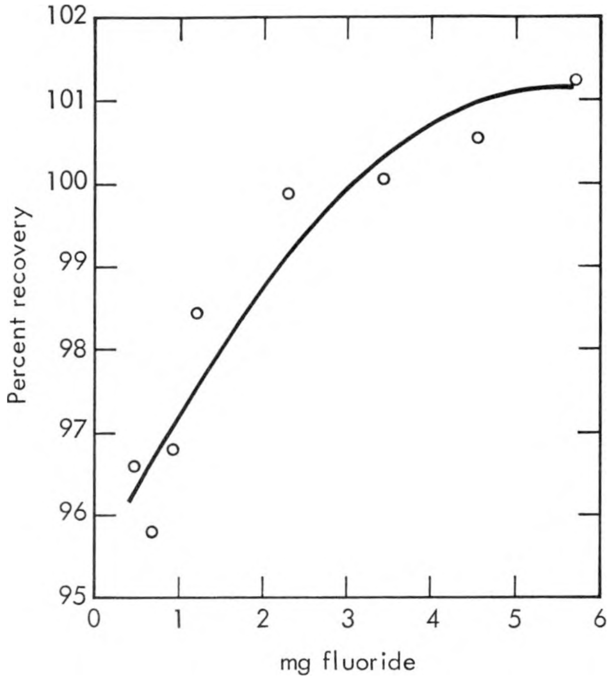

Fig. 2. Recovery of fluoride (standardized against 2.28 mg).

Table I. Recovery of fluoride.[a]

mg F$^-$ Taken	mg F$^-$ Recovered	% Recovery
0.457	0.441	96.50
0.685	0.657	95.91
0.914	0.885	96.83
1.142	1.125	98.51
2.284	2.281	99.87
3.427	3.429	100.06
4.569	4.594	100.55
5.711	5.782	101.24

[a] Standardized against 2.284 mg fluoride.

Table II. Analysis of FEFO in Round-Robin sample No. 1.

	% FEFO by thorium nitrate-methyl-thymol blue method[a]	Lanthanum (III) specific ion electrode method
	2.46	2.32
	2.39	2.32
	2.41	2.40
	2.42	2.34
	2.37	2.31
	2.27	2.33
	2.48	
	2.43	
Average	2.40	2.34
Standard deviation	0.06	0.03

[a] Data obtained by three installations (Lawrence Radiation Laboratory, Livermore; Holston Army Ammunition Plant, Kingsport, Tenn.; Mason and Hanger-Silas Mason Co., Inc., Pantex Plant, Amarillo, Tex.)[17]

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