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CHLORINE, AND FLUORINE

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ABSTRACT

The oxygen flask combustion followed by ion selective electrode measurement has been found to be the most suitable from the point of view of elegance and simplicity for the determination of chlorine and fluorine in actinide complexes. The method has been found to be particularly suitable for glove box adaptation. This report describes the determination of chlorine and fluorine in several uranium complexes, some plutonium complexes and organic analytical standards by this method. The precision and accuracy of the measurements in the milligram level has been found to be quite satisfactory.

INTRODUCTION

Organic elemental analysis has been virtually revolutionised since 1955 by the application of the oxygen flask method for the decomposition of organic materials. It is a very rapid and simple method and in these two respects it can scarcely be bettered. The technique has had a chequered history until its revival in 1955. Since then, a large amount of literature has accumulated and numerous procedures have become available for determining almost any nonmetallic element in organic materials by decomposing the substance in an oxygen filled flask and subsequent determination by a suitable method appropriate to the element in question.

APPARATUS AND GENERAL METHOD

Schöniger(1) in 1955 used combustion in an oxygen filled flask for microanalysis and his procedure has become known particularly in American papers as the Schöniger method, but earlier workers used to call it the oxygen flask method. The apparatus consists of a conical flask fitted with a ground glass stopper into which is sealed a length of platinum wire. To the end of the wire is attached an oblong platinum gauze which acts as a support to clamp the sample container. The sample is weighed onto a piece of filter paper which is folded and clamped on the gauze leaving a protruding fuse which serves as the ignition point. The flask is charged with a suitable absorption solution and flushed with a fast flow of oxygen for a minute. The fuse is ignited and the stopper

immediately inserted into the flask which is simultaneously inverted so that the absorption solution forms a seal around the stopper. Combustion is complete in a few seconds during which the stopper is held firmly to contain the pressure generated. The flask is then shaken for 3-4 mts. and left undisturbed for upto one hour to ensure complete absorption. Thereafter, the stopper is removed and rinsed together with the gauze and wire. The solution is then ready for analysis by some suitable method. For adapting this method for glove box use with radioactive materials, the combustion is accomplished remotely by using a focussed heating beam from a projector bulb having a red filter. It is imperative to use a black paper for encapsulating the sample which can easily be ignited by the projector beam. Methods for the determination of chlorine and fluorine by using specific ion electrodes which are as simple and convenient as the combustion of the sample itself are described in this report.

Determination of Chlorine

In early semimicro methods, (2,3,4) water alone was used as the absorbent, but Schöniger (1) found it necessary to use 10 ml. of 0.2 N potassium or sodium hydroxide solution with 3 drops of hydrogen peroxide for complete absorption on the micro scale. Others (5,6) however have preferred an alkaline bisulphite solution; an ammoniacal peroxide solution (7) has also been used. Satisfactory results, have, however been obtained on the micro scale by absorption in water alone. Corner has found it necessary to add carbon to the alkaline absorption solution (8).

In our experiments, we have been able to get satisfactory results on the semimicro scale by absorption in 20 ml. of water containing about 20 mg. of active charcoal. The role of charcoal is to convert any chlorine or chlorine oxides formed to hydrogen chloride as per the following reactions.



Many methods of estimating the chloride in the solution have been used with varying success. Schöniger (1) uses the Viebock titration involving mercuric oxycyanide. Direct argentimetric titrations with Variamine Blue B (9) or dichlorofluorescein (10) as indicator and the indirect Volhard method have been applied. Also, titration with .004 N silver nitrate in nonaqueous media in presence of dithizone as indicator has been reported (5). Potentiometric (8,12), coulometric (13) and polarographic methods (4) have been suggested as well as a spectrophotometric method (14) based on the reaction of chloride with mercuric chloranilate. Instrumental methods involving transference of the absorption solution as do all the procedures mentioned above negates the simplicity of decomposition by the oxygen flask combustion. Losses during transference of the solution is possible. In addition, such procedures are cumbersome when dealing with radioactive materials inside glove box.

We have incorporated an oxygen flask igniter inside a glove box which uses a projector lamp with a red filter to ignite the sample. The chloride content of the sample is thereafter estimated using a combination chloride sensitive electrode.

Procedure: An accurately weighed sample containing about one milligram of chloride was decomposed in the oxygen flask and the products of combustion absorbed in 20 ml. of water containing about 20 mg. of active charcoal. After 45 mts. the ionic potential of the solution was measured using a chloride sensitive combination electrode (Orion Model 96-17 B) using an Orion 701 A Ionalyser after adding one ml. of 1.0 M NaNO_3 as low level ionic strength adjustor. The amount of chlorine was computed from calibration graph using at least three standards and the percentage of chlorine in the sample calculated. Alternatively, the chlorine contents can also be estimated using a standard solution using the expression,

$$C_2 = C_1 \times 10^{(E_1 - E_2)/S}$$

where E_1 and E_2 are the potentials in relative millivolts of the standard as well as the sample solutions respectively, C_1 and C_2 their respective concentrations and S , the electrode slope. The electrode slope was ascertained from the difference in potential of two standard solutions which differ by a decade in concentration of interest. The following samples analysed by this method are listed in the accompanying tables.

DETERMINATION OF FLUORINE

There is little concordance between the different results by this method for fluorine. Schöniger (1) absorbs the products of combustion in water and titrates the fluoride with cerous nitrate in the presence of murexide as indicator for which the end points are not sharp. Rogus and Yasuda (15) use a colorimetric finish with ferric salicylate. The main difficulty experienced by several workers have been the incomplete combustion of the sample which were to some extent overcome for monofluorinated compounds by mixing 20 mg. of sodium peroxide with the sample. However, Belcher, Leonard and West (16) have found difficulty in the decomposition of trifluorinated compounds and recommend that the sample be mixed with potassium chlorate instead of sodium peroxide before combustion. Volatile compounds containing trifluorinated groups pose great difficulty due to the partial volatilisation of sample before the combustion zone before decomposition. Our results on the analysis of TTA complexes gave a value of fluorine which is 10-15% lower than the theoretical. Mixing the sample with sodium peroxide or potassium chlorate or both didn't improve the results. However, dramatic results were obtained when the combustion products were absorbed in water containing active charcoal. This proves that as in the case of chlorine some decomposition products of fluorine other than hydrogen fluoride are produced on combustion which are not absorbed but which get converted to HF in the presence of charcoal.

Satisfactory results have been obtained for TTA complexes of uranium and plutonium by this method. The method has also been used for determining fluoride impurity of oxide fuels in the ppm range.

Procedure: An accurately weighed sample containing about one mg. fluoride mixed with 10 mg. of potassium chlorate was ignited in the oxygen flask and the products of combustion absorbed in 20 ml. of water containing 20 mg. of active charcoal. The addition of potassium chlorate is particularly important in the decomposition of compounds containing trifluoromethyl groups. After allowing to stand for 45 mts., the potential of the solution was measured using a fluoride ion combination electrode (Orion 96-09) after adding 20 ml. of TISAB-II buffer using an Orion 701A Ionalyser. The fluoride content was computed from a calibration graph using at least three standards of 0.01M NaF and the percentage of fluorine in the sample evaluated. Alternatively the fluoride content can also be estimated using the expression,

$$C_2 = C_1 \times 10^{(E_1 - E_2) / S}$$

where E_1 and E_2 are the potentials in relative millivolts of the standard as well as the sample solutions, C_1 and C_2 their respective concentrations and S , the electrode slope. The electrode slope was computed from the difference in potential of two solutions having a decade change in concentration. The accompanying tables show the samples analysed by this method.

In conclusion, it is felt that the determination of chlorine and fluorine in actinide complexes by specific ion electrodes matches in simplicity, elegance and convenience their decomposition by oxygen flask combustion. This technique has been found to be ideally suited for actinide complexes under glove box conditions.

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TABLE-1

Chlorine in p-chlorobenzoic acid
% Cl = 22.65

Weight of sample(mg)	Potential of Std. 10^{-3} (mv)	Electrode Slope(S)	Potential of sample(mv)	Net Cl (mg)	Cl (%)
5.46	73.8	57.9	60.2	1.1994	21.97
5.97	73.8	57.9	56.9	1.3704	22.96
7.71	75.2	58.4	51.6	1.7804	23.09
6.21	75.2	58.4	57.0	1.4351	23.11
6.64	75.4	58.5	56.1	1.4977	22.56
6.10	75.4	58.5	57.5	1.4163	23.22
4.34	75.4	58.5	66.2	0.9998	23.04
4.74	75.4	58.5	64.2	1.0834	22.86
5.13	74.1	58.1	60.8	1.1828	23.06
4.78	74.1	58.1	62.5	1.1044	23.10

Blank = 0.0200 mg.

Mean Cl % = 22.90 \pm 0.37
Precision = 1.63 %; Error = + 3.3%

TABLE-2

Chlorine in 5-chloro-8-hydroxyquinoline
% Cl = 19.75

Weight of sample (mg)	Potential of solution, mv	Amount of chloride from graph, ppm (net)	% Cl
12.50	87.5	2440	19.52
10.20	90.0	2070	20.29
5.00	107.4	1000	20.00
8.75	96.0	1670	19.09
10.50	88.8	2150	20.48
10.93	88.3	2080	19.03
6.30	105.1	1220	19.37
6.30	105.0	1200	19.05
8.25	98.3	1500	19.39

Blank = 0.0200 mg.

Mean % Cl = 19.58 ± 0.55

Precision = ± 2.8 %; Error = -0.86 %

TABLE-3

Chlorine in Benzyl-Isothiourea hydrochloride
% Cl = 17.49

Amount of sample(mg)	Potential of solution, mv	Amount of chloride from graph, ppm(net)	% Cl
7.20	99.6	1250	17.36
8.45	95.0	1490	17.63
9.05	93.2	1600	17.68

Blank = 0.0200 mg.

Mean % Cl = 17.56 ± 0.17

Precision = ± 0.98 %; Error = - 0.4 %

TABLE-4

Chlorine in Tris-triphenyl phosphine rhodium monochloride
 % Cl = 3.83

Amount of sample(mg)	Potential of solution, mv	Amount of chloride from graph, ppm(net)	% Cl
23.45	109.4	950	4.05
18.65	116.5	700	3.75
17.45	118.0	665	3.81
26.00	109.3	970	3.73
17.25	118.2	650	3.77
16.20	120.0	625	3.86
17.20	119.0	655	3.81
15.35	123.0	560	3.65
14.15	124.6	520	3.68
14.15	122.5	560	3.96
15.30	120.5	620	4.05

Blank = 0.0200 mg.

Mean % Cl = 3.83 \pm 0.14
 Precision = \pm 3.6; Error = 0.0 %

TABLE-5

Chlorine in Dicaesium plutonium hexachloride (Cs_2PuCl_6)
 % Cl = 29.67

Amount of sample (mg)	Potential of std (10^{-3}) mv	Electrode slope (S)	Potential of sample (mv)	Amount of Cl (net) mg	% Cl
3.19	71.5	57.2	63.7	0.9359	29.39
4.50	71.5	57.2	55.3	1.3269	29.49
3.99	71.8	56.4	58.6	1.1810	29.64
4.30	71.8	56.4	57.0	1.2632	29.38
3.76	71.9	56.4	60.0	1.1181	29.74
3.36	71.9	56.9	62.1	0.9777	29.20
3.30	71.5	56.9	62.8	0.9736	29.51
4.06	71.5	56.9	57.4	1.2202	30.06
3.94	72.2	57.0	59.5	1.1499	29.22
3.19	72.2	57.0	63.6	0.9689	30.38

Blank = 0.036 mg.

Mean % Cl = 29.60 \pm 0.37

Precision = \pm 1.26 %; Error = -0.13 %

TABLE-6
Fluorine in p-Fluorobenzoic acid
% F = 13.56

Amount of sample (mg)	Potential of Std (10^{-3})mv	Electrode slope, (S)	Potential of sample (mv)	Amount of F (net) mg	% F
5.17	1.0	59.4	-9.2	0.7052	13.64
6.48	1.0	59.4	-14.8	0.8761	13.52
4.97	30.4	59.3	22.2	0.6531	13.14
7.21	30.2	59.3	12.1	0.9592	13.30
4.99	30.2	59.4	22.3	0.6527	13.08
4.78	30.6	59.4	22.3	0.6553	13.71
5.94	28.9	59.4	16.0	0.7832	13.18
4.88	28.9	59.4	21.0	0.6452	13.22
3.86	28.5	59.4	26.2	0.5194	13.46
5.11	28.5	59.4	19.9	0.6636	12.98

Blank = 0.0020 mg.

Mean F % = 13.32 \pm 0.25
Precision = \pm 1.8 %; Error = -1.8 %

TABLE-7

Fluorine in $\text{UO}_2(\text{TTA})_2\text{TBP}$
 $\% \text{ F} = 11.66$

Amount of sample, mg	Potential of std. (10^{-3})	Electrode slope(S)	Potential of soln(mv)	Amount of F(net)mg.	% F
5.12	29.1	59.2	23.4	0.5929	11.58
5.94	29.1	59.2	20.2	0.6715	11.30
5.83	29.4	59.2	20.9	0.6611	11.34
4.98	29.4	59.2	24.4	0.5770	11.59
4.51	29.4	59.2	27.4	0.5134	11.38
4.47	29.3	59.1	27.2	0.5155	11.53
3.71	29.3	59.1	31.2	0.4309	11.61
7.69	28.7	57.6	13.8	0.8617	11.21
6.98	28.7	57.6	15.6	0.8019	11.49
8.40	29.3	57.5	12.0	0.9496	11.31
6.24	29.3	57.5	19.0	0.7175	11.50

Blank = 0.0020 mg

Mean % F = 11.44 \pm 0.14

Precision = \pm 1.2 %; Error = -1.9 %

TABLE-8
 Fluorine in $\text{UO}_2(\text{TTA})_2 \cdot \text{DOSO}$
 $\% \text{ F} = 11.56$

Amount of sample, mg.	Potential of std. (10^{-2}) mv	Electrode slope (S)	Potential of soln (mv)	Amount of F (net) mg.	% F
4.21	29.3	57.5	29.2	0.4769	11.33
5.18	29.3	57.5	23.4	0.6016	11.61
6.39	29.0	57.0	18.2	0.7348	11.50
4.69	29.0	57.0	26.0	0.5362	11.43
5.53	29.1	56.9	21.3	0.6513	11.78
6.28	29.1	56.9	18.4	0.7324	11.66
5.22	29.1	56.9	23.0	0.6080	11.65
7.30	29.1	56.9	14.8	0.8473	11.61
6.12	29.1	56.7	19.1	0.7130	11.65
4.85	29.1	56.7	24.8	0.5656	11.66

Blank = 0.0020 mg.

Mean F % = 11.59 \pm 0.13
 Precision = \pm 1.1 %; Error = +0.26 %

TABLE-9

Fluorine in synergistic uranyl and plutonyl complexes

Compound	Amount of sample (mg)	Potential of soln (mV)	Amount of F (net) mg.	% F	
				obt.	Theo.
PuO ₂ (PMTFP) ₂ .DHSO	5.13	23.5	0.5638	11.00	11.05
	4.70	25.5	0.5209	11.09	
PuO ₂ (PMTFP) ₂ .DOSO	5.25	28.9	0.5289	10.12	10.46
	6.37	24.5	0.6383	10.02	
UO ₂ (TTA) ₂ .DCH18C6	7.00	16.0	0.7586	10.84	10.52
	6.83	16.4	0.7468	10.94	
UO ₂ (PMTFP) ₂ .DCH18C6	5.73	23.4	0.5781	10.09	9.62
	6.65	19.0	0.6783	10.20	
UO ₂ (PMTFP) ₂ .DPSO	6.86	15.8	0.7646	11.15	11.22
	5.94	20.6	0.6337	10.67	
UO ₂ (PMTFP) ₂ .DISO	5.50	21.4	0.6110	11.11	11.37
	6.82	15.2	0.7782	11.47	
UO ₂ (PMTFP) ₂ .DSSO	5.96	20.4	0.6623	10.78	10.77

Blank = 0.0020 mg.

PMTFP = 1-phenyl-3-methyl-4-trifluoroacetyl pyrazolone-5

TTA = Thenoyl trifluoroacetone

DCH18C6 = Dicyclohexano-18-crown-6

DHSO = Dihexyl sulphoxide

DOSO = Dioctyl sulphoxide

DISO = Di-isoamyl sulphoxide

DSSO = Di-septyl sulphoxide

TBP = Tributyl phosphate

TABLE-10

Fluoride in Pu(TTA)₄
% F = 19.96

Amount of sample mg.	Potential of std(10 ⁻³)mv	Electrode slope(S)	Potential of soln(mv)	Amount of F(net)mg.	% F
6.55	34.1	59.0	2.2	1.3176	20.12
4.90	34.6	59.5	11.1	0.9435	19.21
5.95	34.6	59.5	5.3	1.1809	19.81
5.40	35.4	59.2	8.5	1.0807	20.01
5.52	35.4	59.2	9.1	1.0557	19.13
6.63	34.4	59.8	2.6	1.2908	19.48
7.37	34.4	59.8	-0.3	1.4435	19.59
4.02	34.2	59.5	15.6	0.7789	19.40
4.09	34.6	59.4	14.4	0.8294	20.30
5.88	34.6	59.4	5.8	1.1584	19.72

Blank = 0.0020 mg.

Mean F % = 19.68±0.39
Precision = 2.0 %; Error = 1.4 %

TABLE-11

F (ppm) in UO_2 samples
Theoretical F = 21.4 ppm.

Amount of sample mg.	Potential of std. (0.0969 ppm)mv	Potential of soln. (mv)	Amount of F (ppm)
106.86	194.8	184.8	19.6
98.02	..	189.2	16.2
108.28	..	180.9	23.5
80.50	..	189.1	19.9
134.36	192.3	178.0	19.3
113.08	..	181.5	19.0
94.36	..	184.2	19.5
81.60	192.0	183.9	22.6
99.25	..	180.6	22.4
150.52	..	171.8	23.0

