Chlorination of Mixed Silver Halides in Gooch Crucibles.

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Any two of the three halogens, chlorine, bromine, and iodine, in the form of their salts, may be determined in a mixture of these salts by the familiar indirect, gravimetric method. This procedure consists of the following steps: precipitating the two halogens together in the form of their silver salts; drying and weighing as such in a Gooch crucible; chlorinating the weighed residue in order to replace the bromine or iodine, or both, and thus converting this residue to silver chloride; and the weighing of the latter salt. Then from the weights of sample, mixed silver halides, and the resulting silver chloride, it is possible to calculate the percentage of the halogens in the sample.

As an example of an indirect analysis, the determination of one pair of the three halogens is included in the course on general quantitative chemical analysis as given in this laboratory. The scheme employed[1] for the chlorination of the mixed silver halides has been to transfer the weighed residue, along with the asbestos in the Gooch crucible, to a boat. The boat was then placed in a hard glass tube, where it could be heated with a burner when necessary, and chlorine passed through the tube until a constant weight was obtained, indicating a complete conversion to silver chloride. This procedure necessitates at least four weighings: the sample, the mixed silver halides, the boat and contents before chlorination, and the same after chlorination.

One distinct liability for error in the process just described lies in the transfer of the asbestos and mixed silver halides from the Gooch crucible to the boat. It is often a difficult matter to obtain a quantitative transfer of the halides, especially when a film clings to the inside surface of the crucible. Small pieces of asbestos in the holes in the crucible may be neglected, since it is necessary to transfer only those portions upon which are liable to be found the particles of silver halide.

With the aim of avoiding the troublesome transfer of the contents of the crucible to the boat, the above procedure has been modified so as to chlorinate the mixed halides directly in the crucible. The scheme adopted for class work consists in placing the Gooch crucible inside a larger crucible, covering the latter with a watch glass having a hole in the center and with the convex side up, and bringing chlorine in contact with the residue by means of a glass tube extending down through the hole in the watch glass to within about 1 cm. of the bottom of the crucible. To hasten the chlorination the outer crucible may be heated. The bromine or iodine replaced are easily driven out of the inside crucible. They often condense at first on the under side of the watch glass but soon disappear with later heating of the crucibles. It is sometimes well to break up a hard residue by means of a glass rod before chlorination, since it is not as well exposed to the action of the chlorine as when spread out in a boat. The weighings neces-

[1] Mahin—Quantitative Analysis, p. 115 (1919).

sary with this procedure include the sample, the mixed halides, and the remaining silver chloride, one less than with the other procedure.

The modified method is essentially similar to that employed by Treadwell[1] who filters the mixed halides into a weighed Fresenius asbestos filter tube of difficulty fusible glass. The tube and contents are weighed, the halides chlorinated in it, and the tube again weighed.

The results shown in the accompanying table illustrate typical determinations as made using the two schemes of chlorination.

Sample Number	Chlorination in Boat		Chlorination in Crucible	
	%Cl	%Br	%Cl	%Br
1	35.30	27 80	35.58	27.51
	35.29	27.81	35.44	27.57
	35.27	27.56	35.53	27.45
	35.13	27.92	35.42	27.60
2	38.10	24.90	37.90	25.10
	37.82	25.18	38.07	24.80
	37.74	25.14	38.17	24.76
	38 03	25.01	38.10	24.74
	.....	.....	38.10	24.78
	.....	.....	37.96	25.20
	%Cl	%I	%Cl	%I
3	45.63	18.75	45 59	18.91
	45.50	19 07	45.44	18.79
	45.62	18 97	45.50	18.88
	45.70	18.90	.....	.....
4	50.41	12 46	50.20	12.92
	50.33	12.55	50.35	12.72
	50.30	12 63	50.26	12.60
5	52.95	9.71	53.15	9.35
	53.05	9.70	53.17	9.45
	53.08	9.50	53.10	9.50
	52 99	9 60	.....	.....
	%Br	%I	%Br	%I
6	17.01	19.78	17.02	19.74
	16.91	19.36	16.97	19.68
	.....	.....	17.19	19.39

The analyses for sample No. 1 were made by the junior author. The other results have been taken from the reports submitted during 1919 and 1920 by the students in general quantitative chemical analysis. While these analyses do not check as well as might be desired, most indirect, gravimetric methods are subject to rather large errors unless approximately equal amounts of the two constituents are present and the multiplying factors used for the calculation is small. Ashley[2] cites an example where an error of 1 mg in a weighing results in a percentage error of 26.20 for one of the constituents.

Conclusion.

A modification of the method for chlorinating mixed silver halides has been proposed. Its advantage over the method previously employed

[1] Treadwell-Hall—Analytical Chemistry, Vol. II, p. 334 (1915).

[2] Chemical Calculations, p. 190 (1913).

lies in the saving of one weighing, and in avoiding the liability of loss in transferring the asbestos and mixed halides from a Gooch crucible to a boat.

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