

THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

THE CHIEF CAUSE OF THE LOSS OF SULPHURIC ANHYDRIDE AND OF CHLORINE BY INCINERATING SUBSTANCES CONTAINING THESE CONSTITUENTS.

By JAMES O'SULLIVAN, F.I.C.

(Read at the Meeting, June 3, 1914.)

THUDICUM and Dupré, "Origin, Nature, and Varieties of Wine," 1872, referred to the loss of sulphuric anhydride and chlorine when the residues from certain wines were incinerated. At that time analysts who had experience in the estimation of chlorine and sulphuric anhydride in beer were aware that the quantity of either of these found in the ash of the beer was not a correct measure. I also know that analysts from time to time have fallen into this analytical trap, and certified beer to contain "chlorine traces" and an amount of sulphuric anhydride which was practically only one-half of what was present.

Ratcliff (ANALYST, 1907, **32**, 84) drew attention to the discrepancy between the sulphuric anhydride found in vinegar by direct precipitation, and the amount found in the ash, and he states "that this difference cannot be satisfactorily explained on the assumption that the carbonaceous matter reduces the sulphates to sulphides"; he inferred that the phosphate present expels the sulphuric anhydride on ignition. Ratcliff also knew that in the estimation of chlorine it was necessary to add sodium carbonate before charring, and that the sulphuric anhydride should be precipitated direct.

The sulphuric anhydride was estimated by direct precipitation in a genuine hock, which by the Haas method showed no sulphurous acid, in grape wine made with Burton water, and in vinegar, and also in the ash of these, with the following results:

				Grm. per 100 c.c.		
				Hock.	Grape-Wine.	Vinegar.
Direct		0.060	0.089	0.125
Ash		0.062	0.038	0.107
Loss		none	0.051	0.018

426 O'SULLIVAN: LOSS OF SULPHURIC ANHYDRIDE AND CHLORINE

The ash of the hock amounted to 0.281 grm.; it contained carbonate, and its alkalinity was equal to 0.164 grm. K_2O ; the ash of the grape wine and vinegar was alkaline, and contained magnesium oxide, but no carbonate or chloride.

Table I. gives the results in grm. of sulphuric anhydride per 100 c.c. of beer and stout.

TABLE I.

	Beer.				Stout.			
	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
Original gravity ...	1062°	1061°	1061°	1082°	1077°	1076°	1079°	1076°
SO ₃ found by direct precipitation ...	0.130	0.127	0.124	0.124	0.097	0.116	0.114	0.114
In ash ...	0.080	0.069	0.078	0.074	0.034	0.055	0.063	0.063
Loss ...	0.050	0.058	0.046	0.050	0.063	0.061	0.051	0.051

The chlorine was determined in the ash obtained from Beer *d* and Stout *d* in the ordinary way, and also by evaporating 100 c.c. with 10 grms. of lime and incinerating the residue.

		Grm. per 100 c.c.	
		Beer <i>d.</i>	Stout <i>d.</i>
Incinerated in presence of CaO	0.026	0.026
Without CaO	nil	nil
Loss	0.026	0.026

The mineral residues of these beers and stouts contained magnesium oxide, but no carbonate or sulphide.

The alkalinity of the ash from Beer *d* was equal to 0.055 grm. of magnesium oxide, and in Stout *d* to 0.059 grm., and the amount of magnesium oxide found in the ash was 0.048 grm. and 0.047 grm. respectively.

The alkalinity was determined by adding an excess of $\frac{N}{10}$ HCl to the ash, filtering, and titrating the filtrate with $\frac{N}{10}$ potash, phenolphthalein being used as indicator. If the ash of beer or stout is extracted with water and filtered, only about one-tenth of its total alkalinity will be found in the filtrate. It is obvious that in these beers and stouts the amount of chlorine and sulphuric anhydride in the ash is not a measure of the quantities present.

The sulphates present in beer and stout are calcium, magnesium, and chiefly potassium sulphate, and the question arises, which of these sulphates is decomposed, on incinerating, to an extent sufficient to account for the great loss of sulphuric anhydride and chlorine.

Fresenius ("Quantitative Analysis," sixth edition, 1873, p. 745) pointed out "that sulphate of magnesium when exposed in a small platinum crucible for fifteen to twenty minutes to the heat of a powerful blast gas-lamp gave, with dilute hydrochloric acid, a solution in which barium chloride failed to produce the least turbidity." That the destruction of sulphate of magnesium explains the losses in

BY INCINERATING SUBSTANCES CONTAINING THESE CONSTITUENTS 427

chief of the chlorine and of the sulphuric anhydride on incinerating substances containing that salt, the following experiments will show.

Estimations were made by direct precipitation in solutions of different sulphates, and also in the ash from the same quantity of the sulphates, previously mixed with 2 grms. of cane-sugar.

TABLE II.

	(1) CaSO ₄ Solution. SO ₃ Grm.	(2) K ₂ SO ₄ 0·201 Grm. SO ₃ Grm.	(3) MgSO ₄ ·7H ₂ O 0·255 Grm. SO ₃ Grm.	(4) MgSO ₄ ·7H ₂ O 0·255 Grm. SO ₃ Grm.	(5) Na ₂ SO ₄ 0·204 Grm. SO ₃ Grm.
Direct precipitation	0·112	0·096	0·082	0·082	0·117
In ash	0·108	0·095	0·009	0·008	0·110
Loss	0·004	0·001	0·073	0·074	0·007
Loss per cent. ...	3·5	1·4	89·0	90·2	5·9

The weight of ash in Experiment 3, Table II., was 0·054 gm.; its alkalinity, calculated as MgO, amounted to 0·0365 gm.; and the quantity of sulphuric anhydride in the ash, calculated as MgSO₄, amounted to 0·0134 gm., or 0·0365 MgO + 0·0134 MgSO₄ = 0·0499 gm., against 0·054 gm. weighed.

Solutions of the sulphates of calcium and magnesium were each precipitated with phosphate of potassium; the precipitates were dissolved in acetic acid and made up to 100 c.c. In one half of each solution the sulphuric anhydride was determined direct, to the other half 2 grms. of cane-sugar were added, and the residues, after evaporation, incinerated. The sulphuric anhydride was also determined in a mixture of sulphate and phosphate of potassium, and in a similar mixture after subjecting it to the same conditions as in an ash determination. The following results were obtained:

TABLE III.

	(1) CaSO ₄ . SO ₃ Grm.	(2) MgSO ₄ ·7H ₂ O. SO ₃ Grm.	(3) MgSO ₄ ·7H ₂ O 0·393 Grm. SO ₃ Grm.	(4) K ₂ SO ₄ 0·2 Grm. K ₃ PO ₄ 0·24 Grm. SO ₃ Grm.
Direct precipitation ...	0·010	0·064	0·126	0·092
In ash	0·009	0·025	0·037	0·092
Loss	0·001	0·039	0·089	nil
Loss per cent.	10·0	60·9	70·6	nil

If free phosphoric acid is present in a solution containing sulphate, and it is desired to estimate the sulphuric anhydride, the barium precipitate must be repeatedly washed with boiling dilute hydrochloric acid to free it from phosphate. In my experience this is a difficult estimation, unless the phosphoric acid is first converted into a phosphate.

TABLE IV.

Behaviour of Magnesium Sulphate and Potassium Chloride when Ignited.

	Experiment I. Ignited together.	Experiment II. Ignited in Presence of Cane-Sugar.	Experiment III. KCl ignited with Cane-Sugar.
SO ₃ present per cent.	32.3	32.3	—
SO ₃ found „	32.5	13.9	—
Cl present „	47.1	47.1	47.1
Cl found „	5.5	nil	28.4

It is clear from these experiments that the chlorine is lost on ignition with magnesium sulphate, that the sulphuric anhydride is fixed by the potassium, and that in the presence of organic matter (Experiment II.) both sulphuric anhydride and chlorine are lost.

The decomposition of magnesium sulphate on ignition being a question of time and temperature, I have little doubt that had the ignition in Experiment I. been prolonged the whole of the chlorine would have been displaced by the sulphuric anhydride, and the quantity of the latter in excess of what the potassium could fix would also have been lost.

The sulphuric anhydride was estimated in 100 c.c. of a water containing sulphates of calcium and magnesium; in the residue of the same quantity of water after ignition; and in the ash obtained from 100 c.c., to which 4 grms. of cane-sugar were added:

SO ₃ in water direct	Grm.
„ residue ignited	0.076
„ ash	0.076
	0.063

In the experiments in which organic matter was present, the mass was first charred over a bunsen for as short a time as possible, and then incinerated in a muffle.

The conclusions arrived at are—(1) That although chlorides are decomposed and chlorine is lost on incinerating organic substances containing chlorides, the sulphates of calcium, potassium, and sodium, are not appreciably reduced. (2) Magnesium sulphate undergoes decomposition on ignition unless a carbonate is present. In the absence of a carbonate the ash of substances containing magnesium sulphate will, when ignited, consist of magnesium oxide. (3) The quantity of magnesium sulphate in a substance containing chlorides may be sufficient to cause the total loss of the chlorine on incineration.

