A NOTE ON THE DISTILLATION OF PERMANGANIC ACID FROM SULPHURIC ACID SOLUTIONS

by

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The attention of the authors has been drawn to the fact that permanganic acid is present in the vapours from boiling sulphuric acid solutions of concentration exceeding about 7 M. In view of the losses of manganese that might be occasioned by prolonged boiling of such solutions this volatility of permanganic acid has been briefly investigated.

Table I shows the ratio of the molecular concentration of permanganic acid in the vapour evolved from boiling sulphuric acid solutions to the concentrations of manganese in the remaining solution.

Table II shows the ratio obtained in similar experiments with nitric acid.

It will be observed that in the case of sulphuric acid solutions the concentration of permanganic acid in the vapour reaches a maximum with 10 M solutions. The increase in volatilization with increase in acid concentration is almost certainly due to the elevation of temperature, which accounts for the fact that very little permanganate is lost even from concentrated nitric acid. In sulphuric acid solutions more concentrated than 10 M the sudden decrease in volatilization probably results from the rapid formation of permanganic anhydride.

TABLE I

SULPHURIC ACID SOLUTION

Molarity of Sulphuric Acid	Temperature of Solution °C	Molarity of Manganese in Solution $\times 10^4$	Molarity of Manganese in Distillate $\times 10^4$	$\frac{[\mathrm{Mn}] \text{ in the Distillate}}{[\mathrm{Mn}] \text{ in the Acid Solution}}$
5.4	117	7.2	0.06	0.008
6.0	120	8.0	0.17	0.021
6.5	124	8.7	0.56	0.064
7.2	130	9.3	1.45	0.16
8.0	142	10.2	3.5	0.35
8.9	151	10.6	8.5	0.80
10.2	166	10.7	11.6	1.08
11.9	190	11.4	1.4	0.12
14.1	223	13.4	0.6	0.045

TABLE II

NITRIC ACID SOLUTION

Molarity of Nitric Acid	Temperature of Solution °C	Molarity of Manganese in Solution × 10^4	Molarity of Manganese in Distillate × 10^4	$\frac{[Mn] \text{ in the Distillate}}{[Mn] \text{ in the Acid Solution}}$
10.9	121	0.75	Nil	0.00
13.1	122	0.85	0.012	0.014
15.0	124	1.1	0.03	0.027
16.0	125	2.0	0.12	0.060

ANALYTICAL APPLICATIONS

The possibility of employing the distillation of permanganic acid as an analytical procedure for the separation of manganese has been investigated. A solution containing manganese and potassium periodate in 10 M sulphuric acid was boiled vigorously in a distillation flask and the concentration maintained at 10 M by the gradual addition of water from a dropping funnel, the stem of which projected to the bottom of the flask. The permanganic acid in the distillate was determined absorptiometrically.

Trouble was encountered owing to the decomposition of permanganic acid vapour, with deposition of a film of manganese dioxide on the walls of the apparatus. The decomposition could be markedly reduced, however, by adding 40% v/v nitric acid instead of water. This ensured that the permanganic acid distilled in an acid atmosphere. Despite this precaution, deposition still occurred and thorough cleaning of the glass surfaces of the distillation unit was necessary before each distillation.

EXPERIMENTAL DETAILS

An all glass apparatus was employed, consisting of a 250 ml distillation flask connected to a water condenser. A tap funnel was inserted in the neck of the flask with its stem projecting to within 0.5 cm of the bottom. 50 ml of 10 M sulphuric acid containing about 2 mg of manganese and 2 g of potassium meta-periodate was heated to boiling and 200 ml* of 40 % v/v

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[*] It may be shown that the efficiency of distillation by this method (provided that liquid is added to the flask at exactly the rate at which it is distilled) is given by the expression:

$$w = W\left(1 - e^{\frac{-v.a.}{V}}\right)$$

Where·

w = weight of manganese distilled
W = Initial weight of manganese in the distillation flask
v = Volume of solution which is distilled
V = Constant volume of liquid in the flask
a = The ratio shown in the last column of Tables I and II.

Thus in 10 M sulphuric acid solutions a volume of at least four times V must be distilled before recovery is reasonably complete and it will be seen that the sulphuric acid concentration must be such that the value of 'a' is as great as possible.

nitric acid run in through the tap funnel so that the volume was maintained at 50 ml. The rate of distillation was about 5 ml per minute.

The distillate was diluted to 400 ml and any reduced manganese reoxidized by boiling with potassium periodate.

Solutions with known amounts of manganese added as a standard manganese sulphate solution have been distilled in this manner and the manganese content of two high chromium steels has been determined. (Periodate was added *after* the solution of the steel in 10 M acid). Recoveries are shown in Table III.

TABLE III

Source of Manganese	Amount of Sample Taken Micrograms	Amount of Manganese Found in Distillate Micrograms	Recover as Percentage of Added Manganese
Standard Manganese Sulphate solution	1100	1105	100.5
	2200	2190	99.5
	2200	2210	100.5
	2200	2170	98.5
	Gram		Manganese Found as Percentage
Austenitic Steel 22% Chromium 9% nickel (0.73% manganese)	0.1	730	0.73
	0.1	725	0.725
Free cutting stainless steel (Zirconium selenide type) (0.45% manganese)	0.25	1100	0.44

This method gives satisfactory recoveries but has the disadvantage of being lengthier than alternative procedures. A brief description has been given, however, as it is considered that the method may prove useful under conditions where strongly coloured solutions or turbidities are present or where a preliminary separation of the manganese as manganese dioxide is inconvenient (*e.g.*, for the determination of manganese in certain non-ferrous alloys such as tin or aluminium bronzes).

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SUMMARY

1. If solutions which contain manganese periodic acid and sulphuric acid are boiled, permanganic acid is found in the steam. The concentration of permanganate in the steam is negligibly small until the sulphuric acid concentration of the solution exceeds about 6 M. It is at a maximum when the sulphuric acid is 10 M and then rapidly decreases as the sulphuric acid concentration further increases.

2. The distillation of permanganic acid from nitric acid solutions is inappreciable even from the concentrated acid.

3. A brief account is given of the analytical application of the distillation from 10 M sulphuric acid.

RÉSUMÉ

1. Lorsqu'on porte à ébullition une solution renfermant du manganèse, de l'acide periodique et de l'acide sulfurique, on trouve de l'acide permanganique dans la vapeur produite. La concentration de l'acide permanganique dans la vapeur est peu importante lorsque la concentration de l'acide sulfurique dans la solution est inférieure à 6 M. On atteint un maximum lorsque l'acidité est 10 M, puis il y a diminution rapide au fur et à mesure que la concentration de l'acide sulfurique augmente.

2. Pour les solutions nitriques, la quantité d'acide permanganique qui distille est très faible même quand on emploie l'acide concentré.

3. On expose brièvement les possibilités d'application analytique de la distillation, au moyen de l'acide sulfurique 10 M.

ZUSAMMENFASSUNG

1. Kocht man Lösungen von Mangan, Perjodat und Schwefelsäure, so findet man Permangansäure im Dampf. Die Permanganatkonzentration im Dampf ist gering, solange die Konzentration der Schwefelsäure in der Lösung 6 M nicht übersteigt. Sie ist maximal bei einer Schwefelsäurekonzentration von 10 M und nimmt dann rasch ab, wenn die Schwefelsäurekonzentration weiter zunimmt.

2. Aus salpetersaurer Lösung, auch aus konzentrierten Säuren, destillieren nur unbedeutende Mengen von Permangansäure.

3. Die Anwendung der Distillation aus 10 M Schwefelsäure in der analytischen Chemie wird kurz auseinandergesetzt.

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