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ANALYSIS OF ACIDIC SOLUTIONS CONTAINING HEXAVALENT CHROMIUM

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ABSTRACT

The volumetric method recommended for the estimation of chromic acid-dichromate mixture in a plating solution involves titration of the diluted test solution against standard NaOH using bromocresol green as indicator. This method in the absence of any sharp end point gives inconsistent results. A new method has been worked out in which the free chromic acid is volumetrically estimated by titrating the solution against standard NaOH with the addition of barium acetate and phenolphthalein as indicator. During this titration, the chromate and dichromate present in solution is removed as the insoluble barium chromate. Total hexavalent chromium is separately determined by titration with ferrous ammonium sulphate with n-phenyl anthranilic acid. Suitable methods of calculation were found to give reproducible values in regard to free chromic acid and dichromate in a mixture.

Key words: Analysis, Cr(VI)

INTRODUCTION

In a metal finishing shop, solutions of chromium trioxide and sulphuric acid or of dichromate and sulphuric acid are commonly used. A self regulating chromium plating solution may be composed of chromium trioxide, potassium dichromate and other compounds. During use of these solutions, their chemical balance is disturbed and hence a suitable method of analysing for different ingredients is desirable for their replenishment. Though the solutions can be analysed without any difficulty instrumentally or by a combination of instrumental and volumetric analysis [1], it will be more convenient to make use of volumetric analysis alone. It is, however, difficult to choose an acid-base indicator for use with a chromium trioxide or dichromate based solution, the intense colour of which masks the end-point.

The purpose of this paper is to present a scheme of volumetric analysis of a mixture of chromium trioxide and potassium dichromate in water.

EXPERIMENTAL

Volumetric titrations of solutions of chromium trioxide and potassium dichromate were carried out with standard sodium hydroxide (~ 0.1 N) as titrant, after adding an excess of pure barium acetate to each test solution. Phenolphthalein was employed for detecting the end-point. Titrations were also carried out against a standard solution of ferrous ammonium sulphate (~ 0.1 N) after adding a 10 ml portion of approximately 6N H_2SO_4, and N-phenylanthranilic acid as an indicator.

RESULTS AND DISCUSSION

The addition of barium acetate to a solution of chromium trioxide and/or potassium dichromate produces an equivalent quantity of acetic acid (as shown below) and it is the latter that actually reacts with the alkali introduced from the burette.

$$H_2CrO_4 + Ba(COOCH_3)_2 \rightarrow BaCrO_4 + 2CH_3COOH \quad \ldots (1)$$

$$K_2Cr_2O_7 + 2Ba(COOCH_3)_2 + H_2O \rightarrow$$

$$2BaCrO_4 + 2CH_3COOH + 2CH_3COOK \quad \ldots (2)$$

Equations (1) and (2) show that the equivalent weights of chromium trioxide and potassium dichromate are half of their molecular weights, i.e. 50.0 and 147.1 respectively. In the case of titration with ferrous ammonium sulphate, however, the equivalent weights are one third and one sixth of the respective molecular weights in accordance with the equations

$$CrO_4^{2-} + 3Fe^{2+} + 8H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O \quad \ldots (3)$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad \ldots (4)$$

If t_1 and t_2 are the titre values in the titrations, for example, against 0.1N NaOH and 0.1 N ferrous ammonium sulphate and x and y the quantities of chromium trioxide and potassium dichromate respectively.

$$\frac{x}{40} + \frac{y}{147.1} = \frac{t_1}{10 \times 1000}$$

and

$$\frac{x}{33.33} + \frac{y}{49.03} = \frac{t_2}{10 \times 1000}$$

The values of x and y can be obtained by solving these simultaneous equations.

The results of titrations carried out with mixtures of chromium trioxide solution and potassium dichromate in different quantities are given in Table I. The results show that the titre values are acceptably accurate.

Table I: Analysis of mixtures of CrO_3 and $K_2Cr_2O_7$ in solution

Composition of mixture		Volume of 0.0807 N NaOH	Volume of 0.1000N ferrous solution	Quantity of CrO_3 determined	Quantity of $K_2Cr_2O_7$ determined
CrO_3 (mg)	$K_2Cr_2O_7$ (mg)	(ml)	(ml)	(mg)	(mg)
100.00	–	24.70	–	99.66	–
100.00	49.36	28.75	–	99.66	48.08
100.00	98.72	32.80	–	99.66	96.16
100.00	148.08	37.05	–	99.66	146.60
196.10	49.36	52.50	68.75	194.40	51.15
98.05	24.68	25.70	33.75	95.10	25.46

It is possible to apply the method with a minor modification to analysis of a solution of chromium trioxide and sulphuric acid or of that of chromium trioxide, sulphuric acid and phosphoric acid. In the case of the former, an excess of barium acetate is added and the solution set aside for about 30 minutes and filtered and the filtrate titrated against a standard sodium hydroxide solution with phenolphthalein as indicator, a redox titration being additionally carried out against a standard ferrous ammonium sulphate solution with another sample of the same composition. As the filtrate contains acetic acid, the phenolphthalein end-point denotes neutralisation of all acetic acid. It is felt that in the case of a mixture of CrO_3, H_2SO_4 and H_3PO_4 in water, titration to methyl orange end-point of the filtrate obtained after addition of an excess of barium acetate will give the quantity of phosphoric acid. With methyl orange for end-point detection, only one third of phosphoric acid should be considered to have reacted. The phenolphthalein end-point corresponds to two thirds of phosphoric acid and all chromum trioxide and sulphuric acid together as equivalent to acetic acid. The redox titration gives, of course, the quantity of chromium trioxide. While the first four experiments (Table I) may suggest the possibility of dispensing with the redox titration, titrations are required to be carried out both against alkali and ferrous solutions. The results for mixtures of $K_2Cr_2O_7$ with 100.00 mg of CrO_3 are actually based upon the differences in titre values with NaOH as titrant due to $K_2Cr_2O_7$ additions.

It appears that tetrachromate chromium plating solutions can also be analysed as described in this paper.

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