

ΑΝΑΛΥΤΙΚΗ ΧΗΜΕΙΑ.— **Gravimetric determination of thiocyanate ions in the presence of chloride or bromide ions**, by *John K. Kouinis - Theodore F. Zafiropoulos* *. Ἀνεκρινώθη ὑπὸ τοῦ Ἀκαδημαϊκοῦ κ. Γ. Τσατσᾶ.

INTRODUCTION

Most of the analytical methods of the thiocyanates can be classified into two major groups: those based on conversion to sparingly soluble and/or coloured thiocyanates; and those in which the thiocyanate ion undergoes oxidation.

There has, always, been interest in analysis of mixtures of halides and pseudohalides, including thiocyanates. León [1] determined thiocyanates in the presence of bromides, by potentiometric titration with silver nitrate. Parida et al [2] reported the determination of thiocyanates in chloride and thiocyanate mixtures by potentiometric titration, using a Ag/AgSCN electrode. Grey and Cave [3] carried out the determination of thiocyanates in mixtures containing chlorides, bromides and iodides, employing high frequency titration with silver nitrate. Borroughs and Attia precipitated triocyanates, in the presence of bromides, as CuSCN, with copper acetate in an ammoniacal solution of the sample, containing ascorbic acid as a reducing agent. No cuprous bromide is precipitated. The precipitate is dissolved in nitric acid/ ferric alum and the thiocyanate ions are titrated potentiometrically with a silver nitrate solution. Recently, Chadwick [5] found that thiocyanate (also iodide, borate, perchlorate and other anions) was precipitated by 2, 4, 6-triphenylpyrylium chloride in dilute hydrochloric acid, offering the possibility of gravimetric determination.

EXPERIMENTAL

The gravimetric determination of thiocyanates as palladium thiocyanate, Pd(SCN)₂, by the method of PdCl₂, was tested and applied during a research project on complex compounds containing thiocyanates.

* ΙΩΑΝΝΟΥ Κ. ΚΟΥΤΙΝΗ - ΘΕΟΔΩΡΟΥ Φ. ΖΑΦΕΙΡΟΠΟΥΛΟΥ, Σταθμικός προσδιορισμός τῶν θειοκυανικῶν ἰόντων παρουσία χλωριούχων ἢ βρωμιούχων.

For the evaluation of the method and the establishment of its reliability and accuracy, solutions of potassium thiocyanate and potassium bromide, of accurately known concentrations, were prepared. The solution of palladous chloride, PdCl_2 , is prepared by dissolving 1 gram of the compound in 100 ml concentrated hydrochloric acid (12 M) and diluting the resulting solution to 500 ml with deionized water.

To a series of solutions, containing thiocyanates in amounts ranging from 5 to 20 mg and bromides in amounts up to 25 mg a slight excess of palladous chloride solution is added slowly and with constant stirring. The solutions are set aside, for two hours, to insure complete precipitation and digestion of the precipitate. The formation and settling of the precipitate commence a few minutes after the addition of the PdCl_2 solution. The precipitates are, subsequently, filtered in porcelain crucibles and washed a few times with small portions of deionized water. The precipitates are heated, for one hour, at 110°C and weighed. The process of heating and weighing is repeated, until a constant weight is obtained.

The accuracy of the method, established by the statistical analysis of a large number of samples (over thirty) is $\pm 0.70\%$.

The method, just described, is simple and relatively fast. In contrast to the methods of Instrumental Chemical Analysis, it does not require special equipment or apparatus and the cost of the reagent, palladous chloride, can be decreased, significantly, by the recovery of palladium from the precipitates and filtrates. The table below shows the results of the statistical analysis. The authors will continue work for further improvement of the method.

TABLE I

No. of determinations	Amt of SCN^- (mg) taken	Amt of SCN^- (mg) found	Relative Error (%)
15	5.80	5.76	-0.69
5	8.70	8.67	-0.34
5	11.60	11.64	+0.34
8	17.40	17.50	+0.57

ΠΕΡΙΛΗΨΙΣ

Ἡ παροῦσα ἀνακοίνωσις ἀναφέρεται εἰς τὸν σταθμικὸν προσδιορισμὸν τῶν θειοκυανικῶν ἰόντων, παρουσία χλωριούχων ἢ βρωμιούχων ἰόντων, διὰ τῆς καταβυθίσεως τούτων ὡς θειοκυανικὸν παλλαδίον, $\text{Pd}(\text{SCN})_2$, εἰς ὄξινον δι' ὑδροχλωρικοῦ ὀξέος περιβάλλον.

Διὰ τῆς μεθόδου αὐτῆς προσδιορίζονται ποσότητες θειοκυανικῶν ἀπὸ 5 ἕως 20 mg, παρουσία χλωριούχων ἢ βρωμιούχων ἰόντων εἰς ποσότητας ἕως καὶ 25 mg διὰ τὴν περίπτωσιν τῶν βρωμιούχων.

Ἡ μέθοδος ἐδοκιμάσθη καὶ ἀκολούθως ἐφηρμόσθη κατὰ τὴν διάρκειαν ἐρευνητικῆς ἐργασίας συμπλόκων ἐνώσεων, αἱ ὁποῖαι περιεῖχον καὶ θειοκυανικά ἰόντα. Αὕτη εἶναι ἀπλή καὶ, σχετικῶς, ταχεῖα. Ἐν ἀντιθέσει πρὸς τὰς μεθόδους τῆς ἐνοργάνου χημικῆς ἀναλύσεως, ἡ μέθοδος δὲν ἀπαιτεῖ εἰδικὰς συσκευὰς ἢ σκευή, τὸ δὲ κόστος τοῦ χλωριούχου παλλαδίου δύναται νὰ μειωθῇ διὰ τῆς ἀνακτίσεως τοῦ παλλαδίου ἐκ τῶν ἰζημάτων καὶ δηθημάτων.

Ἡ ἀκρίβεια τῶν ἀποτελεσμάτων, ὡς προκύπτει ἐκ τῆς στατιστικῆς ἀναλύσεως ἰκανοῦ ἀριθμοῦ δειγμάτων (τριάνκοντα καὶ πλέον), εἶναι $\pm 0,70\%$.

BIBLIOGRAPHY

1. C. Léon, Compt. Rend. **233** 170 (1951).
2. R. N. Parida - S. Aditya - B. Prosad, J. Indian Chem. Soc., **29**, 377 (1952).
3. P. Grey - G. C. B. Cave, Can. J. Chem. **42**, 770 (1964).
4. J. E. Borroughs - A. I. Attia, Anal. Chem. **40**, 2052 (1968).
5. T. C. Chadwick, Anal. Chem. **45**, 985 (1973).