Ὁ κ. Καλογερέας ἀποδίδει τὴν ὑπὸ τῶν ἐρευνητῶν τοῦ ἐλαίου τοῦ Bitondo παρατηρηθεῖσαν αὔξησιν τῶν στερεῶν λιπαρῶν ὀξέων εἰς τὴν πρόωρον πτῶσιν τῶν ἐλαιῶν συνεπείᾳ τῆς προσβολῆς αὐτῶν ὑπὸ τοῦ δάκου. Ὡς δὲ ἡ ἔρευνα τοῦ κ. Καλογερέα ἔδειξεν, ἐφ' ὅσον ἡ ὡρίμασις προχωρεῖ, ἐπὶ τοσοῦτον ἡ περιεκτικότης εἰς στερεὰ λιπαρὰ ὀξέα ἐλαττοῦται καὶ ἡ εἰς ρευστὰ αὐξάνεται. Τοῦτο καταφαίνεται ἐκ τοῦ εἰς τὴν ἀνακοίνωσιν προσηρτημένου πίνακος ἀναλύσεων δειγμάτων ἐλαίων, προερχομένων ἐκ διαφόρου βαθμοῦ ὡριμάσεως ἐλαιῶν. Ἐκ τοῦ πίνακος τούτου συνάγεται ὅτι ἡ ἐλάττωσις τῶν στερεῶν λιπαρῶν ὀξέων ἐκτείνεται διὰ τὸ αὐτὸ μὲν δένδρον ἀπὸ 13,60 ἕως 10.93%, διὰ διάφορα δὲ δένδρα, καὶ δὴ διαφόρων ποικιλιῶν, ἀπὸ 18.01 ἕως 10.93%.

Εἰς τὰ αὐτὰ ἀποτελέσματα, ὅσον ἀφορᾷ εἰς τὴν μεταβολὴν τῆς εἰς λιπαρὰ ὀξέα περιεκτικότητος κατὰ τὴν πρόοδον τῆς ἀναπτύξεως, εἶχον καταλήξει προηγουμένως ἄλλοι ἐρευνηταί, ὡς οἱ Nichols καὶ Friar, οἱ ὁποῖοι εὗρον διακυμάνσεις τοῦ δείκτου ἰωδίου τοῦ ἐλαίου κατὰ τὰ διάφορα στάδια ὡριμάσεως ἀπὸ 79,50 ἕως 94.75 (Fruit Products Journal, August 1939, New York). Ἡ διαφορὰ αὕτη τοῦ δείκτου ἰωδίου δεικνύει ὅτι κατὰ τὴν ὡρίμασιν τῶν ἐλαιῶν ἐπέρχεται μετάπτωσις τῶν στερεῶν λιπαρῶν ὀξέων εἰς ρευστὰ λιπαρὰ ὀξέα, τὰ ὁποῖα αὐξάνονται, τῶν στερεῶν ἐλαττουμένων.

ΧΗΜΕΙΑ.— Ascorbic acid (Vitamin C) as an analytical reagent. IV. Detection of molybdenum, by ***E. C. Stathis****, presented by Mr. *C. Zenghelis*.

The reduction of molybdic acid to form a blue solution was tested by many authors for the detection of various elements.

Osmond reported in 1887 the reduction of phosphomolybdic acid with stannous chloride[1].

Zenghelis applied the reaction for the volumetric determination of iron and tin and for the detection of hydrogen[2].

In 1920 Denigès modified the conditions to make the reaction more nearly quantitative and since that time a large number of further modifications have been published.

Recently the detection of vitamin C with phosphomolybdic acid was reported by Bezssonoff[3].

Based on these considerations and on our previous works[4] we have

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* ***Ἐλευθερίου Κ. Στάθη,*** Τὸ ἀσκορβινικὸν ὀξὺ (Βιταμίνη C) ὡς ἀντιδραστήριον εἰς τὴν ἀναλυτικὴν χημείαν. IV. Ἀνίχνευσις μολυβδαινίου.

[1] ***Osmond***, Bull. Soc. Chim. biol. 47 (1887), 745.

[2] ***C. Zenghelis***, Ber. 34 (1901), 2046.

[3] ***Bezssonoff***, Chem. Zentr. IV (1923), 566.

[4] ***E. C. Stathis***, Praktika Academy of Athens, volumes 1942, 1943.

sought to use ascorbic acid as a reagent for the detection of molybdenum.

EXPERIMENTAL

By adding an aqueous solution of ascorbic acid to a solution of sodium molybdate, acidified with phosphoric acid, a blue colour appears on warming.

The reaction is probably due to the reduction of molybdic acid.

When the concentration of molybdenum is less than 0.0002 gr. in 5 ml., the sensitivity of the reaction is depressed and the colour is no more visible.

In order to increase the sensitivity of the reaction various tests were carried out.

It was observed, that if the solution of sodium molybdate is acidified with hydrochloric acid and mixed with sodium phosphotungstate, a violet colour is produced, at room temperature, after the addition of the reagent.

For the detailed investigation of the reaction the following solutions were prepared :

1) Aqueous solutions of sodium molybdate (Na_2MoO_4).
   (A) solution 0.200 gr. of Mo in 100 ml.
   (B) solution 0.020 gr. of Mo in 100 ml.
   (C) solution 0.002 gr. of Mo in 100 ml.
2) Aqueous solution of sodium phosphotungstate ($Na_2O.P_2O_5\ 24WO_3$).
   1.4 gr. of sodium phosphotungstate SCHERING
   ($Na_2O.P_2O_5 24WO_3+27H_2O$) in 100 ml.
3) Solution of hydrochloric acid.
   1 part of hydrochloric acid sp. gr. 1.19 to 1 part of water.
4) Aqueous solution of ascorbic acid.
   0.1 gr. of ascorbic acid in 100 ml.

The tests were conducted, at room temperature, in the usual test tubes.

By mixing 1 ml. of (A) solution with 2 ml. of water, 0.5 ml. of hydrochloric acid, 0.5 ml. of sodium phosphotungstate and adding 1 ml. of ascorbic acid, a violet colour is produced immediately.

The colour intensity varies with the concentration of molybdenum present.

A control test was carried out by mixing 3 ml. of water, 0.5 ml. of hydrochloric acid, 0.5 ml. of sodium phosphotungstate and adding 1 ml. of ascorbic acid, none colour appeared even after a long time.

The test may be made quantitative by comparing the colour with the colours produced by operating in a similar manner on known amounts of molybdenum.

The results obtained by the above method are given in the table 1.

The method as given above has been found especially useful for the detection of molybdenum in special steels and molybdenum ores.

TABLE I

Milliliters of Molybdenum sol.	Ml. of H_2O	Ml. of HCl	Ml. of $Na_2O.P_2O_5\,24WO_3$	Ml. of the reagents	Colour of the reaction	Molybdenum in grams
IA	2	0.5	0.5	1	violet	0.002000
0.5A	2.5	0.5	0.5	1	»	0.001000
0.25A	2.75	0.5	0.5	1	»	0.000500
IB	2	0.5	0.5	1	»	0.000200
0.5B	2.5	0.5	0.5	1	light violet	0.000100
0.25B	2.75	0.5	0.5	1	»	0.000050
IC	2	0.5	0.5	1	»	0.000020
0.5C	2.5	0.5	0.5	1	»	0.000010
0.25C	2.75	0.5	0.5	1	»	0.000005

The following procedure was adopted in the analysis of a high-speed steel.

1.5 gr. of the drillings are dissolved in hydrochloric acid on the water bath. The hot solution is treated with the minimum amount of nitric acid required to oxidise the molybdenum (2 ml. will suffice) and evaporated to dryness. The residue is taken up in hydrochloric acid and gently heated to expel oxides of nitrogen. A yellow residue is due to WO_3. The liquid is diluted with water and WO_3 is removed by filtration, and washed.

The filtrate is heated and then sodium hydroxide solution is added to impart a slightly alkaline reaction. The formed precipitate is filtered off and the filtrate containing molybdenum is received in 100 ml. volumetric flask and diluted with water to the mark.

For the detection of molybdenum 1 ml. of the above solution is mixed with 2 ml. of water, 0.5 ml. of hydrochloric acid and 0.5 ml. of sodium phosphotungstate. After the addition of 1 ml. of ascorbic acid a violet coloration is produced.

The sample of steel which has been used for the detection of molybdenum, analyzed by the usual analytical methods has been found to contain:

Tungsten 15.5 %, Chromium 3.5 %, Vanadium 2.0 %, Molybdenum 0.8 %.

The procedure adopted in the analysis of an ore containing molybdenite (MoS_2) has as follows:

From the finely powdered sample 2 gr. are treated in a beaker with 50 ml. of concentrated nitric acid on the water bath. After 10',50 ml. of concentrated hydrochloric acid is added and the mixture is evaporated to dryness. The residue is taken up in concentrated hydrochloric acid and the evaporation is repeated nearly, but not quite, to dryness. The syrupy liquid is treated with hot water and then sodium hydroxide solution (2N) is added to impart an alkaline reaction.

The formed precipitate is filtered off, washed with water and the filtrate is transferred in 100 ml. volumetric flask.

1 ml. of the above solution is mixed in a test tube with 2 ml. of water, 0.5 ml. of hydrochloric acid and 0.5 ml. of sodium phosphotungstate; on the addition of 1 ml. of ascorbic acid the presence of molybdenum is revealed by a violet coloration.

The percentage of molybdenum in the analyzed ore has been found by the usual analytical methods 5%.

CONCLUSION

A method has been described for the detection of molybdenum based on the reduction of molybdic acid by ascorbic acid.

From the various experiments carried out it has been proved that the method as given above is especially useful for the detection of molybdenum in special steels and molybdenum ores.

ΠΕΡΙΛΗΨΙΣ

Νέα μέθοδος ἀνιχνεύσεως μολυβδαινίου περιγράφεται, ἥτις στηρίζεται ἐπὶ τῆς ἀναγωγῆς τοῦ μολυβδαινικοῦ ὀξέος ὑπὸ ὑδατικοῦ διαλύματος ἀσκορβινικοῦ ὀξέος.

Ἡ εὐαισθησία τῆς ἀντιδράσεως καὶ ἡ σταθερότης τῆς ἐμφανιζομένης χροιᾶς τὴν καθιστοῦν ἐφαρμόσιμον εἰς τὸν χρωματομετρικὸν προσδιορισμὸν τοῦ μολυβδαινίου.

Ἡ ἐφαρμογὴ τῆς μεθόδου εἰς τὴν ἀνάλυσιν χάλυβος ταχείας δράσεως ὡς καὶ εἰς τὴν ἀνάλυσιν μεταλλευμάτων μολυβδαινίου ἔδωκεν ἱκανοποιητικὰ ἀποτελέσματα.

Βασιλ. Βαλαώρα καὶ Στρ. Παπαϊωάννου. Τὸ ἀνάστημα καὶ τὸ βάρος τῶν Ἑλλήνων μαθητῶν κατὰ τὴν περίοδον τοῦ πολέμου.
