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# Short Communications

## A Simplified Method for the Colorimetric Determination of Molybdenum in Steel

E. KNUTH-WINTERFELDT

*Dansk Industri Syndikat's Testing Laboratory, Copenhagen, Denmark*

The starting point for this investigation was an article about colorimetric determination of molybdenum in steel by Kapron and Hehman[1]. In this it was shown that an addition of butyl cellosolve (2-butoxyethanol) had a stabilizing effect on the red-brown molybdenum-thiocyanate complex; the proposed analysis procedure gives very reliable results and represents a decided step forward, but is somewhat circumstantial in regard to the final colouring of the steel solution.

By observations made with butyl cellosolve the present author got the idea that it might be possible to make a stable solution containing butyl cellosolve, potassium thiocyanate and stannous chloride at the same time; the colouring of the final solution might then be effected by mixing fixed amounts of this single reagent and the dissolved sample, thus simplifying the colouring process considerably.

Investigation did not bear out this idea completely, but sufficiently so for practical purposes, as the mixed reagent may be used for at least two months; the butyl cellosolve has a strongly retarding effect on the reaction between potassium thiocyanate and stannous chloride, but does not stop it.

The following procedure was set up:
*Special reagents:*

*Perchloric acid-phosphoric acid:* 1 volume of perchloric acid, 70 %, + 2 volumes of phosphoric acid, 85 %, + 3 volumes of water.

*Perchloric acid-sulphuric acid:* 1 volume of perchloric acid, 70 % + 1 volume of conc. sulphuric acid.

Mixed reagent for the blank solution *(blank reagent):*

a) 100 g stannous chloride is dissolved at less than 50° C in conc. hydrochloric acid; after cooling, water is added, while stirring, until the total volume is 1 litre. 24 hours later the solution is filtered, and 1-2 g granulated tin are added; it is kept under $CO_2$-atmosphere.

b) 800 ml sulphuric acid (50 %) is mixed with 600 ml butyl cellosolve and cooled.

c) Add 1400 ml b) to 800 ml a), while stirring, and cool. Add 1-2 g granulated tin and keep under $CO_2$. This solution is very stable.

d) *The blank reagent* is made by adding 100 ml water to 1100 ml c). Add 1-2 g tin and keep under $CO_2$. Very stable.

Mixed reagent for the colour reaction *(colouring reagent):*

e) 4 g potassium thiocyanate is dissolved in 100 ml water. Very stable.

f) *The colouring reagent* is made by adding 100 ml e) to 1100 ml c). Add 1-2 g granulated tin and keep under $CO_2$. It may be used for about 2 months.

*Analytical procedure:*

1. *Low-alloy steels (and carbon steels).* *Gently* dissolve 0.5 g of the sample in a

mixture of 5 ml hydrochloric acid (19 %) and 15 ml perchloric acid (70 %), heat to dense fumes and boil for 5 minutes. Cool until a precipitate begins to form, add about 50 ml water, boil a short time, cool to room temperature, transfer to a 250 ml volumetric flask, dilute to the mark and mix thoroughly. (During the above procedure the silicic acid has been quantitatively precipitated: it may be removed by filtering and directly used for a determination of the silicon content; in this case, however, it is better to dissolve 1 g of the sample.)

If the steel contains more than 0.5 % C or 0.05 % S, dissolve in 5 ml hydrochloric acid (19 %), oxydate completely by dropwise adding conc. nitric acid, boil, cool slightly, add 15 ml perchloric acid (70 %) *etc.*

Pipette 50 ml of the steel solution into a beaker, and, while stirring, 50 ml colouring reagent; five minutes later the solution is ready for measurement; the colour does not change for more than a week, and the solution keeps clear.

The blank solution is prepared by mixing 50 ml steel solution and 50 ml blank reagent. It is not necessary to use pipettes if the steel solution is only faintly coloured in itself.

It is possible to analyse 4 samples in 35 minutes.

2. *High-chromium and stainless steels.* The chromium content is reduced by adding 2 ml conc. hydrochloric acid to the fuming perchloric acid solution (let it cool somewhat before the addition) and boiling until the red-brown chromyl chloride vapours are no longer visible. This process is repeated until a new addition gives only a slight colouring of the fumes. A content of 1—2 % Cr is permissible.

If the sample dissolves with difficulty in the usual manner, proceed in the way described for steels with more than 0.5 % C, reduce the chromium content, etc.

3. *Tungsten steels.* 0.5 g is *gently* dissolved in 20 ml perchloric acid-phosphoric acid. When the solution becomes clear cool slightly, add 10 ml perchloric acid and reduce the chromium content. It is sometimes necessary during this process to add small portions of perchloric acid to compensate for evaporation losses. Add 5 ml perchloric acid-sulphuric acid, fume for 5 minutes, cool slightly, add 50 ml water, boil about 3 minutes, cool to room temperature, transfer to 250 ml volumetric flask, dilute to the mark etc.

It is possible to dissolve in the well-known sulphuric acid-phosphoric acid mixtures, oxydate with nitric acid *etc.*, if care is taken with the driving out of the nitrous gases. As a general procedure the perchloric acid method is preferable, because of the very low blank values for instance.

The above procedure was verified in the following way:

A. The Kapron and Hehman (K & H) method and the present modification (K—W) were compared by measuring the extinction of the same solutions by each method.

Three types of steel were used:

I. 0.40 C— 2.46 Cr— 2.42 Ni— 0.37 Mo
II. 0.46 C— 1.33 Cr— 0.24 V— 0.65 Mo
III. 1.3 C— 4.5 Cr— 2.67 V— 11.88 W— 1.00 Mo

I was dissolved using the high-chromium, II the low-alloy and III the tungsten method.

The measurements were taken on a Lange colorimeter with stabilized light source and green filter (photocell apparatus).

*Table 1.*

| Method | Colour extinction less blank extinction | | |
|---|---|---|---|
| | I | II | III |
| K & H | .199 | .254 | .323 |
| K—W | .199 | .255 | .323 |