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SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN(V) AS THIOCYANATE COMPLEX IN CERTIFIED STEEL MATERIALS

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ABSTRACT. The method is based on the photometric determination of tungsten (V)-thiocyanate complex (420 nm, absorptivity coefficient 35 l g^{-1} cm^{-1}) after the reduction of W(VI) with $SnCl_2$ and $TiCl_3$. The method was applied to determine W in steel samples dissolved in Speacker reagent. The kinetics of the complex development and the interference of Mo on W determination were studied for ratios of Mo:W up to 2:1. The calibration curve was linear in the range 5-25 μg ml^{-1} W, with a correlation coefficient of 0.994 (n=5) and a detection limit of 1μg ml^{-1} W. For a certified content of 17.7% W in steel, the recovery was 99±2% and the relative standard deviation 2% (n=5). The method allows the determination of W in the presence of Mo up to a Mo/W ratio (m/m) of 1/2.

INTRODUCTION

Several spectrophotometric methods for W determination have been elaborated, but their use strongly depends on the nature and composition of the sample. As a refractory element, W is together with Mo a major constituent of rapid steel used in tool manufacturing. Molybdenum and tungsten have similar colorimetric properties and interferes with each other, which makes difficult the quantitation of W in the presence of Mo.

Feigl and Krumholz first determined tungsten with thiocyanate [1] based on the reduction of W(VI) to W(V) with $SnCl_2$ followed by the development of the photometrable yellow W(V)-thiocyanate complex. Within this procedure, the presence of Mo causes a severe interference.

Several modifications have been performed to simplify the determination of W in the presence of Mo in order to avoid the necessity of their separation. One of these procedures implies the use of $SnCl_2$ mixture with $TiCl_3$ [2] as reduction agent. The order of the reagents addition is of paramount importance. Thus, in the first stage Mo(VI) is reduced to Mo(V) and W(VI) to W(V) with $SnCl_2$ in HCl media. An excessive amount of $SnCl_2$ reduces the thiocyanate used subsequently as a complexation agent. As the thiocyanate is added, W(V) and Mo(V) form slight yellow complexes. The addition of titanium (III) chloride complete the reduction of W(VI) to W (V) and the initially yellow W-thiocyanate complex turns into an yellow-green one according to the remarks of Geld and Caroll [3]. They have pointed out that the yellow-green W(V)-SCN^- complex is obtained if thiocyanate is added before the reduction stage (with $TiCl_3$ in this case). The titanium (III) chloride destroys any residual colour due to Mo(V)-SCN^- since Mo(V) is reduced to Mo(III). This procedure could allow the determination of W in the presence of 1.5-4 % Mo, even at a Mo/W ratio of 6/1 [4].

Another method for the simultaneous determination of Mo(VI) and W(VI) without a previous separation is that based on their catalytic effect on the reaction between hydrogen peroxide and iodide and the spectrophotometric determination of iodine-starch complex.

$$H_2O_2 + 2\ KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + 2\ H_2O \qquad (1)$$

The amount of iodine produced in this reaction is proportional to the concentration of Mo(VI) and W(VI). When citric acid is added in the solution, the catalytic effect of Mo(VI) and W(VI) decreases differently as the catalytic effect of Mo(VI) decreases slightly and that of W(VI) decreases rapidly. The method has been employed in a flow injection system (FI) [5, 6]. The determination takes place in two steps. In the first stage the sum of Mo(VI) and W(VI) is determined in the absence of citric acid, by injecting the sample, H_2O_2, KI and starch into an aqueous carrier stream. In the second stage, in a subsequently injected sample, only Mo(VI) is determined in the presence of the citric acid, based on the same principle. Tungsten (VI) is found by difference. The method is rather complex while the correction for the decreasing catalytic effect of the Mo(VI) in the presence of citric acid is necessary.

Determination of the W(V)-thiocyanate complex after a previous separation by extraction was reported too. In this method, the complex is preconcentrated on column filled with Amberlite XAD-1180 resin [7], extracted with N-phenylacetamide in benzene [8] or as a mixed thiocyanate –propericiazine complex in chloroform [9]. In the determination of W (V) as blue W-toluene-3,4-dithiol complex extracted into heptane, the interference of Mo is inhibited but there is interference from Bi or Cu [10].

Spectrophotometric determination methods in which W(VI) developed complexes with rutin in the presence of hexadecyltrimethylammonium bromide [11] or with salicylfluorone [12] were also reported. Most of the interferences due to Al, Fe, Bi, Ti, Mo, Zr, Cr can be overcome by ion-exchange separation of W [11], extraction with dithiol or by masking with EDTA [12].

The determination of W by inductively coupled argon plasma atomic emission spectrometry (ICP-AES) [13 14], atomic absorption spectrometry with N_2O-C_2H_2 [15, 16] is less prone to interferences. Among electrochemical methods direct current polarography [17], differential pulse polarography [18] and stripping voltammetry [19] are used for the determination of W(VI). Another method used for the simultaneous determination of Mo(VI) and W(VI) in minerals and steel after chelatisation with tetracycline is reversed-phase high-performance liquid chromatography [20] and X-ray fluorescence spectrometry [21].

The aim of this paper was to evaluate a classical spectrophotometric method to determine W as W(V)-thiocyanate complex in steel with W in the presence of Mo. Thus, the kinetics of the W-thiocyanate complex development and the interference of Mo were studied. The dynamic range, the limit of detection and the characteristic mass of W as well as the maximum concentration of Mo, which allows the determination of W without interference, were established.

EXPERIMENTAL

Reagents and standard solutions

A 1000 μg ml^{-1} stock solution of tungsten was prepared by dissolving 0.1600 g Na_2WO_4 in 100 ml distilled water.

A 10000 μg ml^{-1} stock solution of molybdenum was prepared by dissolving 1.8400 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 100 ml distilled water.

A 0.5% solution of $SnCl_2$ (m/v) was obtained by dissolving 1 g $SnCl_2\cdot 2H_2O$ in 80 ml 32 % HCl and diluting to 200 ml with distilled water. This solution should be prepared fresh weekly.

A 25% (m/v) stock solution of KSCN was prepared by dissolving 25 g KSCN in 100 ml distilled water.

A $TiCl_3$ solution was prepared by dissolving 0.5 g Ti metallic powder in 30 ml 32 % HCl. The solution was filtrated and diluted to 50 ml with distilled water. This solution should be prepared fresh daily.

Speacker reagent was obtained by mixing 10 ml 85% H_3PO_4 (m/v), 10 ml 98% H_2SO_4 (m/v) and 10 ml distilled water.

In order to study the kinetics of the W(V)-SCN^- complex development, three standard solution with the concentrations of 5, 10 and 25 μg ml^{-1} W in the absence of Mo were prepared. In the optimum conditions for W determination, the chemical interference of Mo was studied, by preparing W solutions (10 μg ml^{-1}) in the presence of 0; 1; 5; 10; 20 μg ml^{-1} Mo. The influence of Mo on the kinetics of complex development was also studied. For this purpose, standard solutions of 10 μg ml^{-1} W in the presence of 0; 1 and 5 μg ml^{-1} Mo were necessary.

An amount of 0.1000 g certified steel sample (E114, C: 0.81%; Mn: 0.35%; Cr: 4.21%; Mo: 0.96%; Co: 4.71%; Si: 0.18%; S: 0.006%; V: 1.58%; W: 17.7%) was dissolved by carefully warming in 12 ml Speacker reagent. The solution was oxidised with concentrated HNO_3 added in drops until the liquid became clear and the present carbides were completely decomposed. The solution was cooled, filtered, then diluted to 50 ml with distilled water. In order to prepare the steel sample to be photometrated, 2 ml of the above solution, 4 ml 85% H_3PO_4 and 32 ml 0.5% $SnCl_2$ were mixed. After 10 minutes, 4 ml 25% KSCN and 2 ml $TiCl_3$ were added and the solution was diluted to 50 ml with 0.5% $SnCl_2$. After another 10 minutes, the sample was photometrated at 420 nm and the percentage of W in steel was calculated from the calibration curve using a simple formula. The calibration curve was obtained using five standard solutions containing W in the range 5-25 μg ml^{-1} in accordance with the following methodology. Appropriate aliquot volumes of tungsten stock solution, 4 ml 85% H_3PO_4 and 32 ml of 0.5% $SnCl_2$ solution were placed in 50 ml volumetric flasks. After 10 minutes, 4 ml of 25% KSCN and 2 ml of $TiCl_3$ stock solution were added to each flask. The solutions were diluted to 50 ml with 0.5% $SnCl_2$ and the green-yellow developed complex was photometrated after 10 minutes.

The blank solution was prepared of 2 ml of the solution obtained by dissolving steel and 4 ml 85% H_3PO_4 diluted to 50 ml with 0.5% $SnCl_2$.

All solutions were prepared using analytical-reagent grade chemicals (Flucka) and distilled water.

Instrumentation. The spectrophotometric measurements were carried out using the single-beam photometer Spekol 20 Karl Zeiss Jena (320-850 nm).

RESULTS AND DISCUSSION

Kinetics study of the complex development

The kinetics of the development of W(V)-SCN$^-$ complex was studied in the absence and presence of different concentrations of Mo. Thus, the absorbance of the complex was measured at 420 nm and various times, respectively, for three solutions containing 5; 10; 25 µg ml^{-1} W. The kinetic curves are shown in Fig. 1.

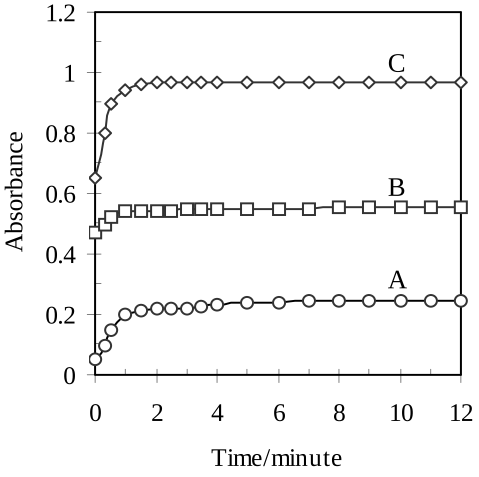

Fig. 1. Kinetic curves for the development of W(V)-SCN$^-$ complex (absorbance measurement at 420 nm) in the absence of Mo for different concentrations of W. A - 5 µg ml^{-1} W; B - 10 µg ml^{-1} W; C - 25 µg ml^{-1} W.

After the prereduction of W(VI) to W(V) with 0.5% $SnCl_2$ in the presence of H_3PO_4 for 10 minutes, 4 ml of 25 % KSCN were added and immediately after that 2 ml of 1% $TiCl_3$. The development of a yellow-green complex was noticed. The solution was diluted to 50 ml and the change in absorbance versus time was immediately measured against blank. For the solution containing 10 µg ml^{-1} W it was studied the influence of Mo on the kinetics of the complex development in the presence of 0; 1 and 5 µg ml^{-1} Mo. The methodology to prepare the solutions was the same. After the prereduction of W(VI) and Mo(VI) to W(V) and Mo(V) with $SnCl_2$, it was added the 25 % KSCN solution. In the presence of Mo, the development of the Mo(V)-SCN$^-$ brick-red complex was observed, which interfered with the complex W(V)-SCN$^-$. After the addition of $TiCl_3$, the Mo(V)-SCN^- complex is decomposed in time, which was noticeable by the disappearance of the brick-red color and the development of the yellow-green complex of W(V). The decomposition of the Mo(V)-SCN^- complex is due to the fact that Mo(V) is reduced to Mo(III), which no more forms a complex with KSCN. As shown by the kinetic curves in Fig. 1, in the absence of Mo the absorbance remains constant after 6 minutes in a diluted W solution (curve A, 5 µg ml^{-1} W). For more concentrated W solutions (curve B- 10 µg ml^{-1} W and C- 25µg ml^{-1} W), the absorbance does not change any more after 2 - 4 minutes. In the presence of Mo (Fig. 2), the absorbance changes slowly during the time as the Mo concentration increases.

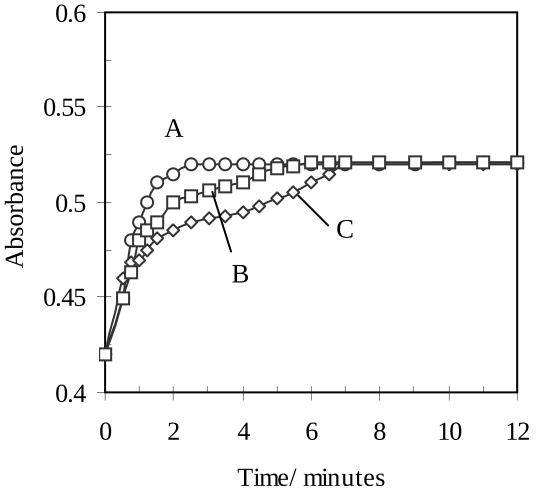

Fig. 2. Kinetic curves for the development of W(V)-SCN^- complex (absorbance measurement at 420 nm) in the presencence of Mo and the same W concentration (10 µg ml^{-1}). A - 0 µg ml^{-1} Mo; B - 1 µg ml^{-1} Mo; C - 5 µg ml^{-1} Mo.

Thus, in the absence of Mo the absorbance becomes constant after 3 minutes (curve A), while in the presence of 1 and 5 µg ml^{-1} Mo the absorbance remains unchanged after 5 and 7 minutes, respectively. After 8 minutes, the absorbance for a constant concentration of W in the presence of Mo in a Mo/W mass ratio in the range 0-0.5 reaches a constant level irrespective of the Mo concentration. The constant absorbance proves the lack of chemical interference of Mo on W determination up to a ratio Mo/W of 1/2. The kinetic study demonstrates that the absorbance of the complex could be measured 10 minutes after $TiCl_3$ is added, a sufficient time interval both for the development of the W-SCN^- complex and the diminishing of Mo(V) interference on W by reduction to Mo(III).

In order to study the interference of Mo on W determination over a wider concentration range, the absorbance of the developed complex was measured for three solutions having the same W concentration (10 µg ml^{-1})

and different Mo concentrations in the range 0-20 μg ml^{-1}.The determinations were carried out according to the following methodology. After the prereduction of samples with $SnCl_2$ for 10 minutes and the development of the W(V)-SCN^- complex subsequently reduced with $TiCl_3$, the absorbance was measured against the blank. The experimental results are presented in Fig. 3. They demonstrate the possibility to determine W in the presence of Mo without any chemical interference up to a mass ratio Mo/W of 1/2.

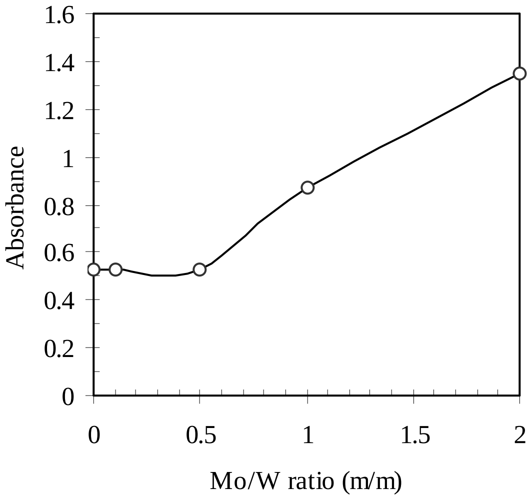

Fig. 3. Interference of Mo on W determination. W: 10 μg ml^{-1}; Mo in the range 0-20 μg ml^{-1}.

For ratios within 1/2 and 2/1 a linear increase of the chemical interference of Mo on W determination is observed. Results equally point out the possibility to eliminate the interference of Mo in W determination by the reduction with $TiCl_3$ to a Mo/W ratio (m/m) of 1/2. The method can not be applied for higher Mo/W ratios. Our results are significantly different from those mentioned in the literature [4], that reports the lack of interference up to a Mo/W ratio of de 6/1.

Analytical performance

In order to assess the analytical performance of the method, the E114 certified steel sample containing 17.7% W and 0.96% Mo was analyzed. The mass ratio Mo/W of 1/20 is within the range free of chemical interference. Our method allows the determination of W in steel up to a concentration of 20% in the presence of around 10% Mo.

The calibration of the spectrophotometer was carried out at 420 nm against the blank prepared as above. The statistical data for the calibration curve and the analytical performance is shown in Table 1.

Table 1.

Calibration results and analytical performance

Wavelength / nm	400
Calibration range [a]/ μg ml^{-1}	5 - 25
R [b]	0.994
$(h \pm s_h)$ [c]	$9\ 10^{-2} \pm 3.6\ 10^{-2}$
$(m \pm s_m)$ [d]	$3.5\ 10^{-2} \pm 0.2\ 10^{-2}$
s_s [e]	$3.5\ 10^{-2}$
γ [f], ml μg^{-1}	1
LOD [g], μg ml^{-1}	1
LOQ [h], μg ml^{-1}	5
m_c [i], μg ml^{-1}	0.12

[a] The number of data for the calibration curve corresponds to five different W concentration (5…25 μg ml^{-1})

[b] Correlation coefficient

[c] h and s_h - intercept and standard deviation, respectively

[d] m and s_m - slope and standard deviation, respectively. The slope of the calibration curve (m) is the calibration sensitivity according to IUPAC [22].

[e] s_s -standard deviation of the regression residual [23].

[f] Analytical sensitivity, $\gamma = m/s_s$ [22].

[g] Limit of detection calculated in μg ml^{-1}; $3/m[s_b^2+s_h^2+(h/m)^2 s_m^2]^{1/2}$ where s_b, s_h and s_m are the standard deviations of the blank, intercept and slope, respectively [24].

[h] Limit of quantitation calculated in μg ml^{-1}as five times limit of detection

[i] Characteristic mass calculated as μg ml^{-1} W in solution; $m_c = 0.004343/m$ [22]

Statistical data from Table 1 show a good reproducibility in all measurements. The limit of detection calculated according to the methodology presented in Table 1 is 1 μg ml^{-1} W that allows a calibration starting from 5 μg ml^{-1} W that corresponds to the limit of quantitation. Thus the method should allow the quantitation of at least 0.25% W in steel. The apparent absorptivity in respect with W calculated from the calibration curve for a 1-cm cell was 35 l g^{-1} cm^{-1}.

The proposed method was applied to the determination of tungsten in a steel reference material with a certified W content (17.7%). The obtained value was 17.5±0.4% which corresponded to a recovery of 99±2 % and a relative standard deviation (n=5) of 2 %. Adopting the null hypothesis, the two-tailed t-test showed that there was no systematic error between the certified and determined W concentration for a 95% confidence interval ($t_{calculated} = t_{critical,\ P=95\%,\ \nu=4}$, 1.11<2.78).

Conclusions

The possibility of the spectrophotometric determination of W as a complex with SCN^- in steel containing Mo was studied. The chemical interference of Mo was eliminated by adding $TiCl_3$. The method allows the determination of W without the interference of Mo up to a Mo/W ratio of 1/2. The limit of detection was 1 $\mu g\ ml^{-1}$ W and the dynamic range was between 5 and 25 $\mu g\ ml^{-1}$. The relative standard deviation was 2 % and the recovery degree for a certified steel sample containing 17.7% W was within 97 and 101 %.

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