Simultaneous Determination of Titanium, Molybdenum and Tungsten with a Synergetic Effect Compensating Flow Injection Multi-standard Additions Method

by W. Jianhua*, H. Ronghuan and Tong Yuehong#

Chemistry Department of Yantai Normal College, Yantai, P.R. China (264025)
#Food Department of Jilin Professional Normal College, Changchun, P.R. China

Key words: flow injection multi-standard additions method, simultaneous determination, spectroscopic analysis, molybdenum, titanium, tungsten

A flow injection spectrophotometric multi-standard additions method had been proposed, and the principle of simultaneous determination for an interfering ternary component mixtures was discussed. The deviations of absorbance from additivity, caused by synergetic effects between the analytes, were compensated with the defined ternary-system synergetic coefficient. The colour reactions of titanium(IV), molybdenum(VI) or tungsten(VI) with cetyltrimethylammonium bromide and salicyl fluoron I were studied, and the conditions for simultaneous determination of them were established. The linear concentration ranges of determination were 0.05–0.35 μg ml⁻¹ Mo, 0.025–0.30 μg ml⁻¹ Ti and 0.25–1.00 μg ml⁻¹ W. Titanium, molybdenum and tungsten contents in a steel and simulated samples were determined, the recoveries for titanium, molybdenum and tungsten were 91.2–105.2%, 92.3–104.7% and 90.6–107.3%, respectively.
Much attention has been paid to development of highly selective procedures for the determination of metallic elements in metallurgy and environmental analytical chemistry. Among the various methods frequently applied, spectrophotometric procedures take still an important part [1-4], but the difficulties are frequently encountered in the cases of determining low concentrations of closely related species, arising from the similarity in their chemical properties, i.e. they interfered seriously with each other, and the separations are difficult and time consuming in most cases. From this point of view, the development of procedures for the determination of analytes in the presence of interferents or for simultaneous determination of binary, occasionally ternary mixtures of closely realted species is of great importance. To this point, the standard additions method [5] has been used with great success. Bosch-Reig and coworkers established a modified standard additions method which they called the “H-Point Standard-Additions Method (HPSAM)” [6,7], by which an unbiased analyte concentration could be obtained in the presence of interferents or by which they could be determined simultaneously when the interferent is known to be present in sample. We recently reported a dual standard additions method [8,9] for determinations of interfering binary mixtures without prior separation.

All the procedures mentioned above can only be used for binary mixtures without synergetic effect. In this paper we report a spectrophotometric multi-standard additions method for the simultaneous determination of ternary mixture. Considering the deviation of absorbance from additivity arising from the synergetic effect of components, we defined a synergetic coefficient for ternary systems. By introducing it into the proposed procedure, the deviation was compensated effectively within certain concentration ranges.

We studied the colour reactions of titanium, molybdenum and tungsten with cetyltrimethylammonium bromide and salicyl fluoron I. The synergetic effects of titanium, molybdenum and tungsten, and the conditions of simultaneous determination were also determined.

We introduced the flow injection analysis (FIA) technique in order to improve the reproducibilities and increase the sampling rate.

The principles of simultaneous determination

Let us consider the components X, Y and Z at concentrations \( C_x \), \( C_y \) and \( C_z \) coexisting in the same sample. They react with a common reagent R to form complexes with absorption maximum close to a certain wavelength. This implies that they interfere seriously with each other during their spectrophotometric determinations, and that there are no synergetic (or mutual) effects.

Adding different concentrations of X (standard series of X) to the solutions containing known concentrations \( C_y^0 \) and \( C_z^0 \) and plotting the analytical signal (absorbance) versus added analyte concentration, \( C_x^{\text{add}} \), two straight lines, \( L_{yx} \) and \( L_{zx} \), can be obtained (Fig. 1a). The intercepts in \( C_x^{\text{add}} \) axis, with respect to the intersection point of X standard series curve \( L_x \) in the same axis, were \( 0A_{y-x} \) and \( 0A_{z-x} \). It is obvious that \( 0A_{y-x} \) and \( 0A_{z-x} \) result from \( C_y^0 \) and \( C_z^0 \), i.e. \( 0A_{y-x} = K_{yx} \cdot C_y^0 \), \( 0A_{z-x} = K_{zx} \cdot C_z^0 \).
Simultaneous determination of Ti, Mo and W...

Similarly, by adding Y or Z standard series to the solutions with known concentrations $C_x^0$, $C_y^0$ or $C_z^0$ respectively, we can obtain two straight lines $L_{xy}$ and $L_{yz}$ by plotting absorbance versus $C_{xy}^{\text{add}}$ (Fig. 1b). Their intercepts in $C_{xy}^{\text{add}}$ axis, with respect to the intersection point of standard series curve $L_y$ in $C_y^{\text{add}}$ axis, were $O_{A_{x,y}}$ and $O_{A_{z,y}}$. Another two lines $L_{xz}$ and $L_{yz}$, and their intercepts in $C_{z}^{\text{add}}$ axis were $O_{A_{x,z}}$ and $O_{A_{y,z}}$ (Fig. 1c). We have $0A_{x,y} = K_{x,y}C_x^0$, $0A_{z,y} = K_{x,z}C_y^0$, $0A_{x,z} = K_{x,z}C_x^0$, and $O_{A_{y,z}} = K_{y,z}C_y^0$.

$K_{i,j}$ are the concentration conversion parameters which represent the intercept in $C_j^{\text{add}}$ axis by unit concentration of component $i$.

In actual determinations we added X, Y and Z standard series to the sample solution respectively, plotted absorbance versus the added concentrations and obtained the intercepts in $C_x^{\text{add}}$, $C_y^{\text{add}}$ and $C_z^{\text{add}}$ axis, $0A_x$, $0A_y$ and $0A_z$. It is obvious that they result from the concentrations of X, Y and Z in the sample, and according to the ordinary standard additions method [5], we have:

\begin{align*}
0A_x &= C_x + K_{y,x}C_y + K_{z,x}C_z \quad (1) \\
0A_y &= K_{x,y}C_x + C_y + K_{z,y}C_z \quad (2) \\
0A_z &= K_{x,z}C_x + K_{y,z}C_y + C_z \quad (3)
\end{align*}

The concentrations of X, Y and Z can be determined by solving equations (1)–(3).

In most actual cases the synergetic effects of ternary mixture result in deviations of absorbance as compared with what is expected from additivity. So it must be considered in actual determinations. From this point of view, we define

\begin{align*}
D_x &= (A - A_y - A_z)/A_x \quad \text{as the synergetic coefficient of Y and Z upon X}, \quad (4) \\
D_y &= (A - A_x - A_z)/A_y \quad \text{as the synergetic coefficient of X and Z upon Y}, \\
D_z &= (A - A_x - A_y)/A_z \quad \text{as the synergetic coefficient of X and Y upon Z},
\end{align*}

\text{i.e.}

\begin{align*}
A_xD_x &= A - A_y - A_z \quad (4) \\
A_yD_y &= A - A_x - A_z \quad (5)
\end{align*}
From eqs. (4) and (5), and (4)-(6), respectively, we obtain:

\[ A_x D_x - A_y D_y = A_x - A_y, \quad i.e. \quad A_y = A_x (D_x - 1)/(D_y - 1) \]  
(7)

\[ A_x D_x - A_z D_z = A_x - A_z, \quad i.e. \quad A_z = A_x (D_x - 1)/(D_z - 1) \]  
(8)

By introducing eqs. (7) and (8) into (4) we have:

\[ A_x D_x = A - A_x [(D_x - 1)/(D_y - 1)] - A_x [(D_x - 1)/(D_z - 1)] \]

\[ i.e. A_x = A [(D_y - 1)(D_z - 1)/(D_y D_z - D_x - D_y - D_z + 2)] \]

Similarly we have:

\[ A_y = A [(D_y - 1)(D_z - 1)/(D_x D_z - D_x - D_y - D_z + 2)] \]

\[ A_z = A [(D_x - 1)(D_y - 1)/(D_x D_y - D_x - D_y - D_z + 2)] \]

So the total absorbance \( (A_{eff}) \) after compensating the synergetic effect may be expressed as:

\[ A_{eff} = A_x + A_y + A_z = A [(D_x - 1)(D_y - 1) + (D_x - 1)(D_z - 1) + (D_y - 1)(D_z - 1)]/[(D_x D_y D_z - D_x - D_y - D_z + 2)] \]  
(9)

Actually, dealing with the total determined absorbance \( (A) \) as in formula (6), the synergetic effects of ternary mixture could be compensated.

**EXPERIMENTAL**

**Reagents**

Titanium(IV) standard solution (3.0 \( \mu \)g ml\(^{-1})\): After dissolving 0.1699 g of TiO\(_2\) in 15 ml H\(_2\)SO\(_4\) (conc.) and 5 g (NH\(_4\))\(_2\)SO\(_4\), the mixture was heated to boil, and diluted to 100 ml; 3.0 ml of this solution was transferred into 1000 ml flask and filled to mark with H\(_2\)SO\(_4\) solution in redistilled water of pH 1.35.

Molybdenum(VI) standard solution, containing 5.0 \( \mu \)g ml\(^{-1}\) Mo(VI), pH 1.35.

Tungsten(VI) standard solution: 10.0 \( \mu \)g ml\(^{-1}\) W(VI), pH 1.35.

Cetyltrimethylammonium bromide (CTMAB) alcohol solution: 1.0 x 10\(^{-2}\) mol l\(^{-1}\), pH 1.35.

Salicyl fluoron I (\( o \)-hydroxyphenylfluorone, SAF) solution: 1.0 x 10\(^{-2}\) mol l\(^{-1}\), pH 1.35.

Carrier solution: dilute H\(_2\)SO\(_4\) solution, pH 1.35.

All solutions above were prepared with chemicals of analytical grade.

**Apparatus and procedure**

For absorbance measurements a 721 type spectrophotometer was used. It was equipped with 10 \( \mu \)l flow cell, connected to a Syntone FIA 2400 analyzer with two peristaltic pumps of 10 channels controlled by a computer (Fig. 2). The inner diameter of polytetrafluoroethylene (PTFE) tube was 0.8 mm, the
Simultaneous determination of Mo and Ly. The length of reaction coils were $L_1 = 100$ mm, $L_2 = 2200$ mm, and the sample loop was 40 µl. The flow rates of all solutions were 2.0 ml min$^{-1}$. The temperature was controlled by a FIA-T01 and JY-501B thermostat, and the pH was measured on a PHS-2 pH meter.

![Diagram](image)

**Figure 2.** The manifold used in the determinations: P$_1$, P$_2$ - peristaltic pumps, V - injection valve, L$_1$, L$_2$ - reaction coils, D - detector, R - recorder, CR - data processing and controlling unit, L$_s$ - sample loop, S - sample solution, C - carrier, R$_1$ - CTMAB solution, R$_2$ - SAF solution, W - waste

The sample solution was transported by a carrier and mixed with SAF solution in L$_1$, the mixture was then mixed with CTMAB solution, and passed through L$_2$ to the detector. The absorbance was measured with respect to the reagent blank, which is predetermined and subtracted automatically by the computer.

**Procedure of the determination**

Titanium(IV), molybdenum(VI) and tungsten(VI) can form ternary complexes with CTMAB and SAF in acidic medium, and their spectra overlap seriously. The wavelength of 520 nm at which the sensitivities for titanium, molybdenum and tungsten were satisfactory was chosen for absorbance measurement.

An orthogonal squares experiment with pH, concentrations of SAF and CTMAB as factors was made at 25°C. With considerations of decreasing memory effect of PTFE tube, improving the reproducibilities, and enhancing sensitivities as far as possible, the following compromise optimal conditions were finally determined: $[\text{SAF}] = 1.25 \times 10^{-4}$ mol l$^{-1}$, $[\text{CTMAB}] = 2.50 \times 10^{-3}$ mol l$^{-1}$, pH 1.35.

**RESULTS AND DISCUSSION**

**Studies on the synergetic effects of titanium, molybdenum and tungsten**

The colour reaction of titanium(IV), molybdenum(VI) and tungsten(VI) with SAF and CTMAB and their synergetic effects were studied within certain ranges under the conditions established above. The synergetic coefficients are listed in Table 1, which shows the following trends:

1. There are only very limited concentration ranges within which the synergetic coefficient is close to unity, i.e. the synergetic effect can be neglected. But it is very difficult to control the concentrations of the ternary mixture within these limited scope in actual determinations, so the synergetic effect must be compensated.
Table 1. The synergistic coefficients at different concentrations

<table>
<thead>
<tr>
<th>Ti concentration</th>
<th>W concentration</th>
<th>0.060</th>
<th>0.150</th>
<th>0.250</th>
<th>0.350</th>
<th>0.450</th>
<th>0.550</th>
</tr>
</thead>
<tbody>
<tr>
<td>µg ml⁻¹</td>
<td>µg ml⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td>0.0625</td>
<td>0.5770 0.9626 0.9790</td>
<td>0.7692 0.8992 0.9042</td>
<td>0.8648 0.9388 0.8545</td>
<td>0.6154 0.9659 0.8409</td>
<td>0.5376 0.8723 0.8268</td>
<td>0.4978 0.8365 0.8284</td>
</tr>
<tr>
<td>0.750</td>
<td>0.625</td>
<td>1.0546 0.9912 1.0711</td>
<td>0.9231 0.8832 0.9682</td>
<td>0.7143 0.8455 0.9150</td>
<td>0.5885 0.8175 0.9202</td>
<td>0.5114 0.7674 0.9305</td>
<td></td>
</tr>
<tr>
<td>0.875</td>
<td>1.000</td>
<td>0.9333 1.0108 0.9763</td>
<td>0.7624 0.9643 0.9604</td>
<td>0.4476 0.9216 0.9214</td>
<td>0.3906 0.9838 0.9540</td>
<td>0.3305 0.8265 0.8865</td>
<td></td>
</tr>
<tr>
<td>0.150</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.375</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.625</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.750</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.875</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Molybdenum concentration, µg ml⁻¹
Simultaneous determination of Ti, Mo and W...
2. The synergetic coefficient changes with the concentration of ternary mixture, but the concentration of each component has different effect upon $D_x$, $D_y$ and $D_z$. At fixed Ti(IV) and Mo(VI) concentration, $D_x$ and $D_z$ decrease, but $D_y$ increases, with the increase of W(VI). Fixing W(VI) at lower Ti(IV) concentration, $D_x$ decreases rapidly with the increase of Mo(VI), but the decrease is much slower at higher Ti(IV) concentration. $D_x$ decreases with the increase of Ti(IV) at fixed Mo(VI) and W(VI) concentration first, and then increases with it.

3. It is obvious that within limited ranges the variations of synergetic coefficient are small. For example, fixing 0.075 $\mu$g ml$^{-1}$ Ti(IV), 0.150 $\mu$g ml$^{-1}$ Mo(VI), and at the range of 0.375–0.875 $\mu$g ml$^{-1}$ W(VI), the changes of synergetic coefficients are $D_x = 0.9670–0.8571$, $D_y = 0.9252–0.9905$, $D_z = 0.9790–0.9091$. Fixing 0.250 $\mu$g ml$^{-1}$ Mo(VI), 0.500 $\mu$g ml$^{-1}$ W(VI), at the range of 0.075–0.300 $\mu$g ml$^{-1}$ Ti(IV), the changes of synergetic coefficient are $D_x = 0.9182–0.9501$, $D_y = 0.7562–0.8354$, $D_z = 0.9308–0.9835$. Similar results are also found within other scales. So the synergetic coefficient could be taken approximately as a constant within certain ranges, and an appropriate value can be chosen for the compensation. This is similar to what we have found for the changes of synergetic coefficients in binary mixtures [10,11].

The determination of $K_{i,j}$ and application of the method

It is decisive to determine accurately the conversion parameters $K_{i,j}$ in equations (1), (2) and (3) for the calculation of the concentrations of the analytes. So dual standard additions were made for known concentrations of $C_{x}^0$, $C_{y}^0$ and $C_{z}^0$, respectively, and all additions were made using the flow injection technique, in order to obtain higher precision. As has been mentioned above the synergetic coefficient is close to unity in limited concentration ranges, i.e. the synergetic effects could be neglected within these ranges. To this point, the added concentrations of titanium, molybdenum and tungsten were all controlled within these limited ranges for determining $K_{i,j}$, so it is not necessary to consider the synergetic effects in these binary mixtures.

The parameters $K_{i,j}$ were determined as $K_{Ti-Mo} = 1.324$, $K_{Mo-Ti} = 0.901$, $K_{Mo-W} = 3.760$, $K_{W-Mo} = 0.273$, $K_{Ti-W} = 4.854$, $K_{W-Ti} = 0.235$. Adding Ti(IV), Mo(VI) and W(VI) standard series to sample solution, plotting absorbance versus the added concentrations, and introducing $K_{i,j}$ into equations (1), (2) and (3), the following working equations were obtained:

$$0 A^0_{w} = C_{w} + 4.854 C_{Ti} + 3.760 C_{Mo} \quad (10)$$

$$0 A^0_{Ti} = 0.235 C_{w} + C_{Ti} + 0.901 C_{Mo} \quad (11)$$

$$0 A^0_{Mo} = 0.273 C_{w} + 1.324 C_{Ti} + C_{Mo} \quad (12)$$

Where $0 A^0_{Ti}$, $0 A^0_{Mo}$ and $0 A^0_{w}$ are the intercepts in $C_{Ti}^{\text{add}}$, $C_{Mo}^{\text{add}}$ and $C_{w}^{\text{add}}$ axis with synergetic effects being compensated.

In actual cases, it is vital to choose an appropriate value of synergetic coefficient for compensation. Obviously, as the analyte concentrations are not known in advance first we can plot the uncompensated absorbance versus the added analytes concen-
Simultaneous determination of Ti, Mo and W...

...tration, $C_{\text{add}}^s$, and obtain the intercepts of the standard addition curves. From that deriving the approximate concentration of analytes in sample, the value of synergetic coefficient could then be chosen accordingly to compensate the absorbance, which was secondly plotted versus $C_{\text{add}}^s$, the intercepts $0A_{\text{W}}^0$, $0A_{\text{Ti}}^0$ and $0A_{\text{Mo}}^0$ in equations (1), (2) and (3) were given for further calculations. It had been confirmed that the error of compensation for absorbance resulting from a slight variation of synergetic coefficient is negligible within narrow ranges for binary mixtures [10,11]. In order to verify that it is also feasible for ternary mixtures, giving two pairs of $D_x$, $D_y$ and $D_z$, deviating significantly from unity, for instance 0.835, 0.779, 0.758; and 0.912, 0.768, 0.645. Supposing a 5% variation (increase) has occurred to each value during the calculation, the results show that the errors for compensation are only about 1.63% and 2.50%, respectively. This is acceptable for most determinations. But if the synergetic effect is very serious, i.e. the errors resulting from compensation are greater than ±5%, the calculated results will deviate from the real concentrations remarkably, and the application of this procedure must be prohibited.

The results of determinations are fairly good within the following concentration-ranges: 0.025–0.30 μg ml⁻¹ Ti(IV), 0.05–0.35 μg ml⁻¹ Mo(VI) and 0.25–1.00 μg ml⁻¹ W(VI).

The influence of foreign ions has been studied in the previous papers [12,13], where more details can be found.

Titanium, molybdenum and tungsten content in a steel and simulated samples were determined, the treatment of samples was similar to that in the previous paper [14]. The results are listed in Table 2.

**Table 2. Results of the determinations (n=3)**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Titanium, mg g⁻¹</th>
<th>Molybdenum, mg g⁻¹</th>
<th>Tungsten, mg g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>known</td>
<td>found</td>
<td>recov., %</td>
</tr>
<tr>
<td>Steel</td>
<td>0.91</td>
<td>0.87</td>
<td>95.6</td>
</tr>
<tr>
<td>Simulated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sample 1</td>
<td>2.32</td>
<td>2.42</td>
<td>104.3</td>
</tr>
<tr>
<td>Simulated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sample 2</td>
<td>1.16</td>
<td>1.12</td>
<td>96.6</td>
</tr>
<tr>
<td>Simulated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sample 3</td>
<td>3.48</td>
<td>3.33</td>
<td>95.7</td>
</tr>
</tbody>
</table>

**REFERENCES**


Received July 1995
Accepted February 1996