SPECTROPHOTOMETRIC DETERMINATION OF MICROAMOUNTS OF Ti(IV) AND Ge(IV) WITH TETRAHYDROXYAZON SN IN THE PRESENCE OF CTMAB LIGAND

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The simple and sensitive spectrophotometric method of determination of titanium(IV) and germanium(IV) is based on the formation of the coloured complex of these metals with tetrahydroxyazon SN (2,2',3,4-tetrahydroxy-3'-sulpho-5'-nitroazobenzene). Optimum concentrations of tetrahydroxyazon SN CTMAB and pH ensuring maximum absorbance were defined. The complex titanium(IV)-tetrahydroxyazon SN-CTMAB and the complex germanium(IV)-tetrahydroxyazon SN-CTMAB show maximum absorbance at 520 and 526 nm accordingly. The molar absorption for titanium(IV) is $(9.37 \pm 0.02) \cdot 10^4$ and the molar absorption for germanium(IV) is $(7.93 \pm 0.03) \cdot 10^4$.

Calibration curves were constructed and statistically evaluated for the cations titanium(IV) and germanium(IV) in the presence of CTMAB is 0-0.8 μg ml⁻¹, RSD-3.1%, and 0-0.6 μg ml⁻¹, RSD-2.5% accordingly. The determination is possible in the presence of Ca(II), Mg(II), Co(II), Ni(II), Be(II), Cd(II), Mn(II), Cr(III), Pb(II), Se(IV), Te(IV), Al(III), Zn(II), La(IV), Br⁻, Cl⁻, I⁻, F⁻, NO₃⁻, CH₃COO⁻, citrates, ascorbic acid and thioure. The method has been applied for the determination of titanium(IV) in the artificial alloys and for the determination of germanium(IV) in the synthetic samples.

Keywords: Titanium and Germanium. Organic reagent; tetrahydroxyazon SN; CTMAB; spectrophotometric determination.

1. Introduction

Important reagents for spectrophotometric determination of titanium(IV) and germanium(IV) include thrifenilmethane dyes in the presence of sulfactants [1-2], pyroqallol in the presence of sulfactants [1-6], and germanium(IV) include dibromophenylfluorene (DBPF) in presence of cetyl-trimethylammonium bromide (CTMAB) [7], phenylfluorene in presence of CTMAB, Trion x-100 and zephiramine [8], 9-(p-fluorophenyl)fluorone of complex cationic surfactants [9], tetrahydroxyazon SN for the determination of these ions in binary mixtures [10], salicylfluorone in the presence of cetylpyridinium [11].

The aforesaid reagents, though sensitive, lack selectivity. Besides being cumbersome, such procedures have inherent sources of errors. The spectrophotometric determination of titanium(IV) and germanium(IV) must be preceded by pre-separation when the two are present together in a mixture as interference is caused due to spectral overlap [1, 3, 6, 11].

Pyroqallol is a widely used reagent for the spectrophotometric determination of several inorganic species [7-10,14-15]. However, there are some simple and rapid
instrumental approaches which allow the simultaneous determination of both complexes with overlapping spectral profiles without prior separation.

In this paper, the influence of cationic surfactants on the spectrophotometric of the complexes of titanium(IV) and germanium(IV) with tetrahydroxyazon SN has been studied. The combination of these effects and the application of the synchronous derivative methodology have allowed the simple resolution of titanium(IV) and germanium(IV) mixtures in real samples.

2. Experimental
2.1. Apparatus
Absorption spectra were recorded on a Shimadzu UV-visible recording spectrophotometer (model UV-260). The pH of the solution was measured on an pH-meter (model pH 350).

2.2. Reagents
Titanium(IV) stock solution, 1.0 mg.ml\(^{-1}\). Preparat by dissolving 0.1003 g of titanium metal (99.98\%) in 10 ml of concentrated sulphuric acid (d = 1.84 g ml\(^{-1}\)) and diluting the solution with water to 100 ml in a calibrated flask. Working solutions were prepared by suitable dilution of the stock solution with 1 M H\(_2\)SO\(_4\).

Stock solution (1 mg ml\(^{-1}\)) of germanium(IV) was prepared by dissolving 1.4409 g of GeO\(_2\) in the water and diluting to 100 ml respectively in water. Working solutions were prepared by suitable dilution of the stock solution with in water.

Solution (1·10\(^{-3}\)M) of tetrahydroxyazon SN. Unless otherwise stated, all reagents used were of analytical grade and their solution was prepared by weighing with distilled water as solvent. The concentration of each reagent was as follows: tetrahydroxyazon SN, 1·10\(^{-3}\) mol.L\(^{-1}\); cetyltrimethylammonium bromide (CTMAB) 1·10\(^{-2}\) mol.L\(^{-1}\).

2.2.1. General Procedure
A get of solutions containing increasing amounts (2 – 40 \(\mu\)g.ml\(^{-1}\)) of titanium(IV) and another one containing increasing amounts (1-30 \(\mu\)g.ml\(^{-1}\)) of germanium(IV) ions, were transferred into a 25 ml calibrated flask each having a fixed amount of 3 ml tetrahydroxyazon SN standart solution (1·10\(^{-3}\) mol L\(^{-1}\)) and 2ml of CTMAB standard solution (1·10\(^{-2}\) mol L\(^{-1}\)). The mixture dilated to a final volume of 25 ml titanium(IV) ion at 0.01M H\(_2\)SO\(_4\) and germanium(IV) ion at optimum pH 4. Immediately afterwards, the absorbance was measured at 520 nm (Ti) and 526 nm (Ge) in a 1.0 cm cell against the reagent in presence of STMAB blanks. After that, dilute the resulting solution to the final solution then keep it for 5 min at room temperature and finally record its absorption spectrum against corresponding reagent blank.

3. Results and discussion
3.1. The effect of pH on the absorbance of the systems
Ti(IV)-tetrahydroxyazon SN-CTMAB and Ge(IV)-tetrahydroxyazon SN-CTMAB complexes in neutral micellar media show pH dependent absorption maximum at 520 and 525 nm, respectively whereas tetrahydroxyazon SN shows maximum absorption at 420 (pH 1-2) and 425 nm (pH 6). As the ligand also absorbs at the \(\lambda_{\text{max}}\) of the complexes, the absorbance due to complex was calculated by taking the differences between the absorbances of the complex and the ligand, each recorded
against water. It was then plotted against pH of the solutions in each case (Fig.1). The graph indicates that complication of titanium(IV) and germanium(IV) commences at 4 and 6, respectively and increases up to pH 1.5-2 and 4. All absorption studies are carried out at these pH values and at 420 and 425 nm, wavelengths of maximum absorption of the complexes in the two cases.

3.1.1. The effect of surfactant

The effect of the presence of cationic surfactant cetyltrimethylammonium bromide Ti(IV) - tetrahydroxyazon SN-CTMAB on the absorption profiles of each system has been studied. Cationic surfactants have a marked effect on the absorbance characteristics of monaro compouds as well as their titanium (IV) and germanium (IV) complexes since cationic surfactants form ternary species of different optical properties as a function of pH.

Without surfactant, the main peak position of Ti(IV) - tetrahydroxyazon SN binary complex 490 nm is in close proximity to that of Ge(IV)-tetrahydroxyazon SN binary complex (486 nm) and in the presence of CTMAB, however, increases not only the sensitivity of both complexes considerably, but also their difference in peak position (520 nm for Ti(IV) and 525 nm for Ge(IV) enlarges markedly (Fig.2). The absorbance value of the titanium(IV) complex at the absorption maximum of the germanium(IV) complex is at 525 nm. This indicates the mixed micellar medium prepared by CTMAB and tetrahydroxyazon SN in an appropriate ratio could be used for the selective and sensitive determination of titanium and germanium in alloys, syntetic samples.

![Fig.1. The effect of pH of binary and ternary on absorbance of Ti(IV) and Ge (IV) complexes tetrahydroxyazon SN. A - Ti(IV)+RSN, 490 nm; B - Ge(IV)+RSN, 485 nm; C - Ti(IV)+RSN+CTMAB, 520nm ; D - Ge+R+CTMAB, 526 nm.](image1)

![Fig.2. Absorption spectra of binary and ternary Ti (IV) and Ge (IV) complexes whis tetrahydroxyazon SN. A - C_R = 8·10^{-5}M, C_{CTMAB} = 2·10^{-4}M, pH 4; B - C_R = 8·10^{-5}M, pH 4; C - C_R = 8·10^{-5}M, C_{Ti}= 2·10^{-5}M, pH 4; D - C_R = 8·10^{-5}M, C_{Ge} = 2·10^{-5}M, pH 6; F - C_R = 12·10^{-5}M, C_{Ti} = 2·10^{-5}M, C_{CTMAB} = 2·10^{-4}M, pH 2; E - C_R = 12·10^{-5}M, C_{Ge} = 2·10^{-5}M, C_{CTMAB} = 2·10^{-4}M, pH 4.](image2)

3.2. Formula at the mixed surfactant solution and its volume

Let the total volume of 1·10^{-3} mol L^{-1} tetrahydroxyazon SN and 1·10^{-2}mol L^{-1} CTMAB be 2.0 ml. Their relative volumes change with an interval of 0.2 ml. With
the decrease of the volume of the CTMAB, the peak height of the titanium(IV) increased rapidly first (from 2.0 to 0.2 ml), which was accompanied by a small red shift of the peak (from 520 to 525 nm) and by a decrease of its half-band width (from 30 to 34 nm). After a slight increase in absorbance (from 2.0 to 1.8 ml), the peak height of the germanium(IV) decreased considerably (from 1.8 to 0.2 ml) with the decrease of the CTMAB, which was accompanied by a small red shift and occurrence of asymmetric peak shape. According to the two requirements mentioned above, the optimum volume ratio should be 1.8 to 0.2 ml (the tetrahydroxyazon SN to the CTMAB). In this ratio, the peak of the titanium(IV) located at 520 nm and Ge(IV) at 526 nm (Fig.2).

Small fluctuation in the volume of the CTMAB (0.05 ml) or the tetrahydroxyazon SN (0.1 ml) had little influence on the resolution and determination. The optimum volume of the mixed surfactant solution prepared in the optimum ratio was 2.0 ±0.4 ml and 0.6 ml of the mixed surfactant solution produced the height in 2.0 ml of such mixed surfactant solution, respectively. The final concentration of CTMAB in the optimum ratio was 8.0·10⁻⁴ mol L⁻¹ and the final concentration of tetrahydroxyazon SN in the optimum ratio was 10·10⁻⁵ mol L⁻¹.

3.2.1. The effect of tetrahydroxyazon SN on the determination

With the increase of the volume 12·10⁻⁵ mol L⁻¹ tetrahydroxyazon SN, the absorbance of the Ti(IV) system (aliquots of 12·10⁻⁵ mol L⁻¹ Tetrahidroxyazon SN +2.0 ml of the mixed surfactant solution +10 µg titanium(IV) of 0.01 mol L⁻¹ H₂SO₄ and 15 µg germanium(IV) +12·10⁻⁵ mol L⁻¹ tetrahydroxyazon SN+ 2.0 ml of the mixed surfactant solution of pH 4.

3.2.2. The effect of temperature and standing time

The absorbance of the Titan(ium(IV)) system decreased with the increase of its temperature especially at higher temperatures (>80⁰C). A decrease in the absorbance of the ternary complex was observed when the temperature was increased to over 80⁰C. The color reactions of ternary complexes of titanium (IV) and germanium (IV) with tetrahydroxyazon SN are instantaneous at room temperature and the absorbance of the complexes remains stable for at >1 day.

3.3. The stoichiometry of the ternary complex

Jobs method of continuous variations was applied to establish the component ratio of the ternary complex. The mole fractions of two of the components were varied continuously, keeping their final combined concentration constant at 4·10⁻⁵ mol L⁻¹ and keeping the third component in a large constant excess (4·10⁻⁴ mol L⁻¹) for all solutions in the series. Under these conditions the ternary system was modified to a quasi binary system [19-21]. The obtained results indicated that the overall ratio for Ti(IV): Tetrahidroxyazon SN:CTMAB was 1:1:1 at pH 2, and Ge:Tetrahidroxyazon SN:CTMAB = 1:2:2 at pH 4. Further confirmation of this ratio was ascertained by applying the molar ratio method using equimolar mixture of tetrahydroxyazon SN and Ti⁴⁺ and Ge⁴⁺ (2·10⁻⁵ mol L⁻¹) as the first partner [22,23]. The experiment was elaborated by keeping the concentration of this mixture constant while changing that of CTMAB (from 0.1 to 12·10⁻⁴ mol l⁻¹) as the second partner, and measuring the absorbance of samples at 520 (Ti) and 526 (Ge) nm against the M(IV)-tetrahydroxyazon SN mixture as a reference blank.
3.3.1. The effect of diverse ions on the determination of the analyte

Interference in the spectrophotometric determination of the titanium(IV) and germanium(IV) from a number of common cations and anions has been investigated in normal as well as derivative modes to evaluate the practical utility of tetrahydroxyazon SN. This was studied by adding the varying amount of the foreign ions (in mg ml\(^{-1}\)) to a solution containing fixed amount of titanium(IV) - 10μg.ml\(^{-1}\) or germanium(IV)-15μg ml\(^{-1}\), tetrahydroxyazon SN, CTMAB and 0.01mol.L\(^{-1}\) H\(_2\)SO\(_4\) and pH 4 accordingly and measuring the change in absorption profiles.

Limiting concentration of the diverse ions that do not interfere in the analysis of titanium (IV) and germanium (IV) ions is summarized in Table 1. The complexation reaction of titanium (IV) and germanium (IV) ions with tetrahydroxyazon SN in the presence of CTMAB media is masked by the presence of tartrate, ascorbic acid, thiocyanide and citrate, respectively. Further, masking agents such as citrate, tartrate and ascorbate have also been used to overcome the interference from a number of cations, but these did not help. Relatively new high order derivative spectrophotometry, has also been used to determine titanium (IV) and germanium (IV) in the presence of interfering ions, as derivatiration of spectra resolves overlapping peaks of normal spectra into separate peaks and troughs, and crossover points.

3.4. The effect of foreign ions and masking agents

The studies of the effect of foreign ions on determination of titanium (IV) and germanium (IV) show, that the selectivity and sensitivity of the method are poor. The tolerated amounts of each ion were taken as those which caused less than a ± 4% alteration in the absorbance. Some interfering species were masked using a masking agent. Ascorbic acid was used as a masking agent. Thus, the selectivity of Fe(III) was increased dramatically in the proposed method. The results of foreign ions are given in Table 1.

As seen from Table 1, the proposed method is more selective sensitivity and for the determination of titan(IV) and germanium(IV) in the presence Cu(II), Cd(II), Pb(II), Co(II), Ni(II), Zn(II), Al(II), Cr(III) and Fe(III). The method which has high sensitivity can be applied to the fast determination of titan(IV) in aluminum-zinc based certified alloys and germanium (IV) in the synthetic samples.

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Ti-R</th>
<th>Ge-R</th>
<th>Foreign ions the presence of CTMAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn (II)</td>
<td>1:370</td>
<td>1:210</td>
<td>1:900</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>1:16</td>
<td>1:55</td>
<td>1:615</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>1:170</td>
<td>1:81</td>
<td>1:1600</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>1:0.5</td>
<td>1:1</td>
<td>1:310</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>1:2</td>
<td>1:1</td>
<td>1:1200</td>
</tr>
<tr>
<td>Co (II)</td>
<td>1:40</td>
<td>1:16</td>
<td>1:1500</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>1:110</td>
<td>1:109</td>
<td>1:1400</td>
</tr>
<tr>
<td>Hg (II)</td>
<td>1:1</td>
<td>1:5</td>
<td>1:140</td>
</tr>
<tr>
<td>Sn (II)</td>
<td>1:0.4</td>
<td>1:1</td>
<td>1:7</td>
</tr>
</tbody>
</table>

Table 1

The influence of foreign ions on complexes Ti-tetrahydroxyazon SN-CTMAB and Ge-tetrahydroxyazonSN-CTMAB absorbance*
Fe (II) | 1:290 | 1:200 | 1:650 | 1:400
Fe (III) | 1:1 | 1:0.5 | 1:1 | 1:1.5
Fe (III)** | 1:50 | 1:40 | 1:510 | 1:290
Al (III) | 1:85 | 1:76 | 1:1270 | 1:950
Cr (III) | 1:10 | 1:42 | 1:1000 | 1:815
Th (IV) | 1:0.7 | 1:39 | 1:18 | 1:3
Zr (IV) | 1:0.1 | 1:0.1 | 1:8 | 1:1
As (V) | 1:0.6 | 1:0.05 | 1:5 | 1:4
Mo (VI) | 1:1 | 1:0.6 | 1:9 | 1:2
W(VI) | 1:2 | 1:0.8 | 1:14 | 1:3
Tartrate | 1:200 | 1:106 | 1:1200 | 1:1300
Urea | 1:300 | 1:180 | 1:1000 | 1:1000
Ascorbic acid | 1:500 | 1:360 | 1:3600 | 1:2000
Sulfo salicylic acid | 1:270 | 1:201 | 1:1150 | 1:800

*Concentration of Ti(IV) = 10 μg, 520 nm and Ge(IV) = 15 μg, 526 nm
**in the presence of ascorbic acid

3.5. Analytical applications

3.5.1. Determination of titanium in aluminium alloys

0.5008 grams of alloys were transferred into a 250 ml beaker and dissolved with 35 ml of an acid mixture [150 ml HCl (d = 1.19g ml⁻¹) +150 ml water +10 ml H₂SO₄ (d =1.84 g ml⁻¹)] by heating. The Fe³⁺ ion in the sample was oxidized by the addition of 1 ml of concentrated HNO₃. The solution was heated until the production of SO₃ vapor stopped. The remaining 10-15 ml part was cooled down and diluted with water in a 200 ml graduated flask. 1-4 ml of it was then transferred into a 25 ml graduated flask for the analysis. After additions of 3 ml 0.5 M ascorbic acid (in order to reduce to Fe(III) into Fe(II) and 3 ml of the aqueous solution of 3 ml1·10⁻³M. tetrahydroxyazon SN reagent, and 2 ml of STMAB standard solution 1.0x10⁻²M colition was made up to the mark with 0.01 M mixture diluted to find H₂SO₄ solution. The absorbance of the solution was measured by UV-visible spectrophotometer at 520 nm against the reagent blank in 1.0 cm path length. The amount of titanium(IV) in the certified alloys was determined by the use of calibration curves. Analysis results of standard alloy samples are listed in table 2. As seen from this table, the recommended method is highly selective and sensitive for the determination of microgram amounts of titanium(IV) in alloys. Relative standard deviations alloys is 1.3%.

Table 2

<table>
<thead>
<tr>
<th>Sample №</th>
<th>Ti% certified value</th>
<th>Ti %, found</th>
<th>RSD%</th>
<th>$\bar{x} \pm ts$ $\sqrt{n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A386-1</td>
<td>0.15</td>
<td>0.157</td>
<td>1.4</td>
<td>0.517±0.003</td>
</tr>
<tr>
<td>M207-4</td>
<td>0.19</td>
<td>0.194</td>
<td>1.6</td>
<td>0.194±0.005</td>
</tr>
<tr>
<td>M207-5</td>
<td>0.32</td>
<td>0.308</td>
<td>1.0</td>
<td>0.308±0.004</td>
</tr>
<tr>
<td>M182-1</td>
<td>0.20</td>
<td>0.205</td>
<td>1.7</td>
<td>0.205±0.004</td>
</tr>
</tbody>
</table>

*Certified value (%): Si -(3-10); Fe -(2-3); Mn -1; Cu -2; Zn -1; Mg, Ni -(0,6); Zr, As - 0.07; Pb -0.2; Be -0.02; Sn -0.01; Al -(85-90): n = 5, p = 0.95
Table 3

Simultaneous determination of germanium in synthetic samples

<table>
<thead>
<tr>
<th>Composition Mg Ge+A+B</th>
<th>Found Mg Ge</th>
<th>RSD% Ge</th>
<th>Recovery% Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1+5.0</td>
<td>1.0</td>
<td>1.2</td>
<td>100</td>
</tr>
<tr>
<td>1+10.0</td>
<td>1.0</td>
<td>0.9</td>
<td>100</td>
</tr>
<tr>
<td>1.0+15.0</td>
<td>1.0</td>
<td>1.3</td>
<td>100</td>
</tr>
<tr>
<td>1.0+20.0</td>
<td>0.98</td>
<td>1.8</td>
<td>98</td>
</tr>
<tr>
<td>1.0+25.0</td>
<td>0.95</td>
<td>2.1</td>
<td>95</td>
</tr>
</tbody>
</table>

a Measured under the same conditions as used for the calibration
b Mean of five replicate determinations

Conclusions

The reaction of titanium (IV) and germanium (IV) with tetrahydroxyazon SN dye in the presence of the cationic surfactant CTMAB is highly selective and sensitive.

Application of cationic substances gives the possibility to increase solubility of titanium-tetrahydroxyazon SN-CTMAB and germanium-tetrahydroxyazon SN-CTMAB complexes in the analysed solution and creates better conditions for the determination.

The results obtained in this work show that the proposed methods for the determination of titanium and germanium in the presence of CTMAB, are applicable to a variety of titan and germanium containing samples and that the methods are simple, selective and accurate.

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Тi (IV) VƏ Ge (IV) İONLARININ MİQDARLARININ TETROHİDROKSİAZON SN İLƏ STMAB İŞTİRAKINDA SPECTROFOTOMETRİK TƏYİNİ

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XÜLASƏ

Titanın (IV) və germaniumun tetrohidroksiazon SN (2,2′,3,4-tetrahidroksi-3′-sulfo-5′-nitroazobenzol) reaktivi ilə rəngli kompleks birləşmələrinin optimal şəraitləri öyrənilmişdir. Ti
(IV)- тетрагидрооксиазон SN ilə STMAB və Ge (IV)- тетрагидрооксиазон SN-STMAB kompleks-larının maksimum absorbsiyası 520 və 525 nm, molyar udma əmsalları isə 9.37±0.02·10⁴(Ti) və 7.93±0.03·10⁴(Ge) uygundur.

Ti IV) və Ge (IV) tayini üçün dərəcəli əyri STMAB iştirakında 0.08 mg ml⁻¹, Sr-3,1% və 0-0,6 mg ml (Ge), Sr=2,5% uyğundur.

STMAB iştirakında kompleksomlagalmayı kanar ionların təsiri öyrənilmişdir Ca (II), Mg (II), Co (II), Ni (II), Be (II), Cd (II), Mn (II), Cr (III), Pb (II), Se (IV), Te (IV), Al (III), La (III), Br⁻, Cl⁻, F⁻, NO₃⁻, CH₃COO⁻, sitrat, askorbin tipəmoçevina təyin maneçilik törəmlər. Metod Ti(IV) ionunun arıntırd və Ge (IV) ionunun səni qarışqlarda tayini əşlənilmişdir.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МИКРОКОЛИЧЕСТВ Ti (IV) И Ge (IV) С ПОМОЩЬЮ ТЕТРАГИДРОКСИАЗОНА CN В ПРИСУТСТВИИ STMAB

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РЕЗЮМЕ

Настоящая работа посвящена спектрофотометрическому методу определения титана (IV) и германия (IV) с образованием цветного комплексного соединения с тетрагидроксизоном SN (2,2',3,4-тетрагидрокси-3'-сульфо-5'-нитроазобензол). Оптимальное условие комплексообразования комплексов Ti (IV) - тетрагидроксизон SN-STMAB и Ge (IV)-тетрагидроксизон SN-STMAB наблюдается при максимальном поглощении 520 и 525 нм. Молярный коэффициент поглощения (9.37±0.02·10⁴ (Ti) и (7.93±0.03·10⁴ (Ge), соответственно. Градуировочный график для определения Ti в присутствии STMAB 0-0,08 мкг/мл, Sr-3,1% и для Ge 0-0,6 мг ml (Ge), Sr=2,5%, соответственно. Избирательность реакции показывает, что определению не мешают ионы Ca (II), Mg (II), Co (II), Ni (II), Be (II), Cd (II), Mn (II), Cr (III), Pb (II), Se (IV), Te (IV), Al (III), La (III), Br⁻, Cl⁻, F⁻, NO₃⁻, CH₃COO⁻, цитрат-ионы, аскорбиновая кислота и тиомочевина. Метод применим для определения Ti в сплавах, а Ge в искусственных смесях.