ANALYTICAL USE OF ARSENAZO III
DETERMINATION OF THORIUM, ZIRCONIUM, URANIUM AND
RARE EARTH ELEMENTS

S. B. SAVVIN
V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry
Academy of Sciences, Moscow, U.S.S.R.

(Received 22 February 1961. Accepted 20 April 1961)

Summary—The reagent arsenazo III (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis(azo-
2)-phenylarsonic acid) gives marked colour reactions with a number of elements. Anions affect the
reaction only to a slight degree and it is possible to work at low pH values; the reaction is very
sensitive and the compound can thus be used for the photometric determination of Th, Zr, Hf, U,
rare earths, and some other elements. The method is most selective for Th, Zr and U\textsuperscript{IV}. Materials
containing these elements can be analysed directly, in the solutions formed after dissolving the sample,
without separation of the stable elements.

AZO-DYES based on chromotropic acid are widely used as reagents for the photometric
determination of various elements. Especially useful and universally applicable are
reagents containing the arsonous group-\text{AsO}_2\text{H}_2. Such a reagent was first prepared
by Kuznetsov\textsuperscript{1} in 1941 and named, in its abbreviated form, "arsenazo". Various
improved analogues of arsenazo were synthesised later and also tested; these included
arsenazo II (which is a double molecule of arsenazo)\textsuperscript{2} and arsenazo III, a bis-diazo
dye based on chromotropic acid and o-aminophenylarsonic acid.\textsuperscript{3} The latter com-
 pound, 1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis([azo-2]-phenylarsonic
acid], is especially suitable for the photometric determination of thorium, zirconium,
uranium\textsuperscript{IV} and of some other elements.

\[
\text{AsO}_2\text{H}_2 \quad \text{HO} \quad \text{OH} \quad \text{AsO}_2\text{H}_2
\]

\[
\text{H}_3\text{OS} \quad \text{N=N} \quad \text{N=N} \quad \text{SO}_3\text{H}
\]

\[
\text{ARSENazo III}
\]

The properties of arsenazo III

Arsenazo III is generally obtained in the form of its disodium salt; it is a crystal-
line, dark-red powder, soluble in water or in weak acids, readily soluble in water which
has been rendered alkaline with sodium bicarbonate or sodium carbonate, and in-
soluble in concentrated acids, or in solutions saturated with sodium chloride, acetone,
alcohol or ethyl ether. The reagent is stable in its dry as well as in its dissolved form;
its properties do not change even when stored for long periods. Oxidising agents
(\text{H}_2\text{O}_2, \text{Cl}_2, \text{Br}_2) and strong reducing agents (\text{Na}_2\text{S}_2\text{O}_3, \text{Ti}^{\text{III}}) attack the reagent;
therefore solutions in which the elements are to be determined must be freed of
oxidising and reducing agents. Usually this does not present any serious difficulties.
The colour of the aqueous solutions of arsenazo III depends on the pH of the medium. The solutions are pinkish or red-crimson coloured, depending on the concentration, within the pH limits of 4 to 10N hydrochloric acid, *i.e.* under conditions usual for the determination of most elements; a 0.01–0.1% aqueous solution of arsenazo III is generally used. In the alkaline region, at pH 5 and higher, a violet or blue colour is observed; the colour is green in concentrated sulphuric acid.

**Colour reactions with elements**

Colour reactions of arsenazo III at various acidities conform to the general rules for the effect of the pH on the colour of the reaction products obtained with colour reagents. Arsenazo III gives colour reactions with many elements (Table I). Its basic characteristic property consists in its ability to form stable chelates; elements can therefore be determined in strongly acidic media and in the presence of sulphates, fluorides, phosphates, oxalates and other complex-forming anions which generally inhibit the direct determination of elements.

**Table I. Colour reactions of arsenazo III**

<table>
<thead>
<tr>
<th>Element</th>
<th>Conditions of determination</th>
<th>Colour of complex</th>
<th>Elements inhibiting the determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent alone</td>
<td>4–10N HCl</td>
<td>Pinkish-crimson</td>
<td>—*</td>
</tr>
<tr>
<td>Th</td>
<td>0.01–10N HCl</td>
<td>Green</td>
<td>Th*</td>
</tr>
<tr>
<td>U IV</td>
<td>0.05–10N HCl</td>
<td>Green</td>
<td>Th</td>
</tr>
<tr>
<td>Zr</td>
<td>0.2–10N HCl</td>
<td>Green</td>
<td>Zr, rare earths, Ca†</td>
</tr>
<tr>
<td>UO₂⁺</td>
<td>pH 4–pH 1</td>
<td>Green</td>
<td>Th, Zr, U, Ca, Cu,</td>
</tr>
<tr>
<td>Sc</td>
<td>pH 4–pH 1</td>
<td>Violet</td>
<td>Th, Zr, U, Ca, Cu,</td>
</tr>
<tr>
<td>Y, La and lanthanides</td>
<td>pH 4–pH 3</td>
<td>Green</td>
<td>Many elements‡</td>
</tr>
<tr>
<td>Bi</td>
<td>pH 4.5–pH 1.5</td>
<td>Violet-blue</td>
<td>Many elements‡</td>
</tr>
<tr>
<td>Pb</td>
<td>pH 5–pH 4</td>
<td>Blue</td>
<td>Many elements‡</td>
</tr>
<tr>
<td>FeIII</td>
<td>pH 3–pH 1.5</td>
<td>Lilac-violet</td>
<td>Many elements‡</td>
</tr>
<tr>
<td>Cu</td>
<td>pH 5–pH 4</td>
<td>Blue</td>
<td>Many elements‡</td>
</tr>
<tr>
<td>Ba</td>
<td>pH 5–pH 4.5</td>
<td>Violet-blue</td>
<td>Many elements‡</td>
</tr>
<tr>
<td>Ca</td>
<td>pH 5–pH 4</td>
<td>Blue</td>
<td>Many elements‡</td>
</tr>
</tbody>
</table>

* In the presence of oxalic acid for masking zirconium.
† In the presence of Trilon B and potassium fluoride, for masking thorium and other elements.
‡ The possibility of selective determination of these elements was not investigated in detail.

Photometric determinations in strongly acidic media are useful in many cases; difficulties caused by the partial hydrolysis of ions of the elements to be determined are eliminated; it is no longer necessary to maintain carefully the pH with the aid of buffer solutions; the selectivity of determination is increased for a number of elements, etc. The slight effect of anions makes it possible to use direct methods of determination in many cases, *i.e.* direct photometric determination can be carried out without separating sulphates, phosphates and other admixtures.

The sensitivity of the colour reactions is of a sufficiently high degree (0.05 to 0.01 μg/ml of the element) when using a spectrophotometer or a photocolorimeter. Quantities of 0.5 μg/ml or more of the element can be determined by visual methods. The methods are most sensitive for the determination of thorium, zirconium, uranium, the rare earth elements and less sensitive for lead, bismuth, iron, copper, calcium, barium.
The high selectivity of the colour reactions is coupled with a well defined contrast in colour transition from pinkish (reagent) to blue or even emerald green (complexes of arsenazo III with elements) and with a high stability of the corresponding arsenazo III complexes; this makes it possible to attain high degrees of dilution without dissociation of the complex. The form of the curves—absorption spectra of the reagent and the complex—is especially important when using photometers. A considerable shift of the absorption spectrum of the complex is observed towards the long wavelengths (compared to the absorption spectrum of the reagent) as well as two sharply defined peaks on the curve of the light-absorbing complex (Fig. 1); this phenomenon makes it possible to attain maximum sensitivity during the determination of the element when working at the optimum wavelengths of 660 to 665 μm. Furthermore, the reagent itself, present in considerable excess during the determination, does not influence the reaction when using this wavelength. A red-light filter is generally used when working...
with photocolorimeters; in this case the excess reagent is eliminated almost completely. The coefficients of molar extinction of some systems are listed in Table II.

**Table II.—Sensitivity of colour reactions of arszenazo III**

<table>
<thead>
<tr>
<th>Element</th>
<th>Conditions of max. sensitivity of reaction</th>
<th>Coefficient of molar extinction, $e^*$</th>
<th>Sensitivity, $\mu g/ml$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spectrophotometer, 50 mm cell</td>
<td>Visual</td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>9N HCl, $\lambda$ 665 $\mu m$</td>
<td>130,000</td>
<td>0-01-0-02</td>
</tr>
<tr>
<td>Zr</td>
<td>9N HCl, $\lambda$ 665 $\mu m$</td>
<td>120,000</td>
<td>0-01-0-02</td>
</tr>
<tr>
<td>Hf</td>
<td>9N HCl, $\lambda$ 665 $\mu m$</td>
<td>$\sim$95,000</td>
<td>0-02</td>
</tr>
<tr>
<td>$U^{IV}$</td>
<td>4N HCl, $\lambda$ 670 $\mu m$</td>
<td>100,000</td>
<td>0-02</td>
</tr>
<tr>
<td>$UO_2^{2+}$</td>
<td>pH 2-0, $\lambda$ 665 $\mu m$</td>
<td>53,000</td>
<td>0-02</td>
</tr>
<tr>
<td>Sc</td>
<td>pH 1-7, $\lambda$ 675 $\mu m$</td>
<td>19,000</td>
<td>0-05</td>
</tr>
<tr>
<td>Y</td>
<td>pH 3-0, $\lambda$ 655 $\mu m$</td>
<td>55,000</td>
<td>0-02</td>
</tr>
<tr>
<td>La</td>
<td>pH 3-0, $\lambda$ 655 $\mu m$</td>
<td>45,000</td>
<td>0-02</td>
</tr>
<tr>
<td>Ce</td>
<td>pH 3-0, $\lambda$ 655 $\mu m$</td>
<td>47,000</td>
<td>0-02</td>
</tr>
<tr>
<td>Gd</td>
<td>pH 3-0, $\lambda$ 655 $\mu m$</td>
<td>58,000</td>
<td>0-02</td>
</tr>
<tr>
<td>Tb</td>
<td>pH 3-0, $\lambda$ 655 $\mu m$</td>
<td>62,000</td>
<td>0-02</td>
</tr>
<tr>
<td>Yb</td>
<td>pH 3-0, $\lambda$ 655 $\mu m$</td>
<td>49,000</td>
<td>0-02</td>
</tr>
<tr>
<td>Zn</td>
<td>pH 3-0, $\lambda$ 655 $\mu m$</td>
<td>43,000</td>
<td>0-02</td>
</tr>
<tr>
<td>Ca</td>
<td>pH 5-0, $\lambda$ 655 $\mu m$</td>
<td>$\sim$10,000</td>
<td>0-05-0-1</td>
</tr>
<tr>
<td>Pb</td>
<td>pH 5-0, $\lambda$ 655 $\mu m$</td>
<td>10,000</td>
<td>0-05-0-1</td>
</tr>
</tbody>
</table>

* Calculated according to the formula $e = \frac{E}{d}$. The method of saturation at excess reagent was used (cf. e.g. Fig. 4). For rare earths, data according to 15.

**Selectivity**

Arsenazo III (Table I) gives colour reactions with many elements and, consequently is not specific for any element.

Its selectivity, i.e. to determine any element in the presence of others, can therefore only be increased by using specific methods. The simplest method appears to be the determination of the required acidity of the solution.

The region of optimum pH values for the interaction of organic colour reagents with elements is known to vary for various elements. The distinct analogy between colour reactions and hydrolysis reactions should be noted. Thus colour reactions with colour reagents are given in strongly acidic media only by those elements whose ions readily tend to hydrolyse: zirconium, hafnium, uranium$^{IV}$, thorium; in mildly acidic media the reactions also yield colours with iron$^{III}$, uranyl ion, rare earths; in mildly acidic media and in neutral media only with: calcium, strontium, magnesium.

Finally, the reaction conditions (optimum pH) are directly related and depend on the nature of the reagents used in the reaction. But for each reagent the ratio of optimum pH values of the reaction with elements remains always constant: easily hydrolysed elements interact in a very acidic medium, stable elements in less acidic media. This also holds true for the reagent arszenazo III.

It can be seen that a high degree of selectivity is attained when determining quadrivalent elements—zirconium, hafnium, thorium, uranium$^{IV}$—with arszenazo III; this reaction can be carried out in strongly acidic media, of the order of 2–10N hydrochloric acid; stable elements do not inhibit the reaction. But the determination of uranium$^{VI}$, rare earths and of other elements is inhibited by many elements.
The degree of selectivity can also be increased by other methods apart from varying the acidity of the mixture. Frequently it is recommended to bind the inhibitors into a colourless stable complex. This is only possible when the element to be determined and the admixtures form with the masking, complex-forming compound—under the given conditions (at defined pH)—complexes which differ markedly in their stability.

The system uranyl ion-Trilon B-stable elements is well-known. Oxalic acid is very useful when determining thorium in the presence of zirconium; the oxalic acid binds the zirconium and has practically no masking effect on the thorium (in a 3–9N hydrochloric acid medium). Fluorides, at pH 2, bind thorium almost completely and do not inhibit the colour reaction of uranyl ion with arsenazo III. Other selective masking, complex-forming compounds can, no doubt, be found.

The selectivity can also be increased by utilising the so-called extraction-photometric methods for the determination of elements; these methods have been described in recent publications. It has been shown that complexes of arsenazo III and elements can be extracted with butyl or amyl alcohol when salts of a heavy organic cation, e.g. diphenylguanidine chloride, are introduced into the solution. In this case direct photometric determination is carried out in the organic phase, without re-extraction. Thus the determination is combined with the simultaneous separation from other, non-extracted elements. The extraction-photometric methods have been investigated for uranium and thorium. They have also been used for zirconium and rare earths but in this case it is preferable to employ more hydrophobic analogues of arsenazo III, e.g. tetrabromo-arsenazo III, which is 1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis[(azo-2)-4,6-dibromophenylarsonic acid].

A high degree of selectivity can be achieved by combining these methods for the determination of thorium, zirconium, hafnium, and uranium. When analysing substances containing large or average concentrations of the above-named elements it is possible to carry out direct determinations in the solutions obtained after decomposing these substances, without separation of the admixtures. Preliminary concentration is required during the analysis of rock-samples and of other materials containing small amounts of the elements. This is achieved by a one-stage precipitation reaction, a single-stage extraction, or similar comparatively simple methods. Complete separation of the admixtures is not necessary—this facilitates the method considerably.

The selectivity is also influenced by a larger or smaller excess of reagent used during the photometric determination. In the latter case, i.e. when the reagent is present in not too large a molar excess with regard to the element to be determined (two-to-three-fold), it will be observed that the degree of selectivity is increased.

**Complex-formation of arsenazo III with elements**

Arsenazo III forms 1:1 complexes with 2+ and 3+ charged cations of elements, e.g. Sr, UO$_2^{2+}$, ZrO$^{2+}$ or La. With 4+ charged cations, e.g. Th, Zr, Hf, U$^{IV}$, the composition may be related to the conditions (pH and the ratio of the components) and E:R=1:1 or E:R=1:2. The composition of complexes of 4+ charged elements is always in the ratio 1:2 under the conditions for colour reactions, when the reagent is present in large excess.

The structure of the complex and the reasons for its unusually high stability will
be described in future communications. It should be noted here that although arsenazo III contains two functional groups:

\[
\text{AsO}_3\text{H}_2 \quad \text{OH}
\]

only one of these groups partakes in the complex-formation with elements. The structure of the complex of uranium VI with arsenazo III, for example, can be depicted as follows:

\[
\text{METHODS FOR THE DETERMINATION OF ELEMENTS}
\]

**Thorium**

The method is perhaps most selective for the determination of thorium. Stable elements do not inhibit the reaction if the ratio of thorium to elements is not in excess of: Zr—1:1,000; UO\(_2^{2+}\)—1:6; rare earths (Ce-subgroup)—1:50; rare earths (Y-subgroup)—1:100; Ti—1:10; Cr\(^{III}\)—1:200; Ni—1:500; Fe\(^{III}\), Pb, Co, Ca, Al and other elements—1:1,000 to 5,000. It was previously pointed out that zirconium can be masked effectively by oxalic acid and that uranium IV readily oxidises to uranium VI. Zirconium is masked most effectively in a 2.5–3.0N hydrochloric acid medium. For every 25 ml of the final solution one has to introduce 6 ml of hydrochloric acid (sp. gr. 1.19), 10 ml of 4% oxalic acid solution and 0.5 ml of a 0.1% aqueous solution of arsenazo III during the photometric determinations. The content of thorium should be 1–25 \(\mu\)g. The measurements are carried out with a spectrophotometer at 665 mm or with a photocolorimeter with a red-light filter. The effect of the acidity on the colour-formation of the thorium arsenazo III complex is shown in Fig. 2.

The methods for the determination of thorium in various substances can be used for the direct determination of thorium as well as for samples with a low thorium-content, after preliminary separation of the admixtures. When analysing rock samples, decompose 0.1–0.5 g of the sample, containing 0.0001% and higher quantities of thorium, supposedly containing 1–25 \(\mu\)g of thorium, with hydrofluoric acid. Evaporate, treat the residue with hydrofluoric acid and wash with water. After filtering, transfer the precipitate to a platinum dish and treat with perchloric acid + hydrochloric acid. After evaporating, dissolve the residue in 1:6 ml of hydrochloric acid (1:1) + 5 ml of water and transfer to a 25 ml volumetric flask. Add ascorbic acid to reduce the iron\(^{III}\) and 10 ml of 4% oxalic acid solution in hydrochloric acid (1:1), 0.5 ml of a 0.1% solution of arsenazo III and dilute to the mark with water. The photometric determination is carried out on a FEK–M with a red-light filter or on a SF–4 at 665 mm in 50-mm cells. The thorium content is found via a calibration curve. Six to 8 determinations can be carried out in 6 hr.
The determination of thorium is not inhibited by substantial quantities of niobium. Thus it is possible to carry out direct determinations of thorium in niobium concentrates after dissolving the sample, without preliminary separation of niobium.\textsuperscript{10} Analysis conditions are essentially identical to those described above.

![Graph: Effect of pH on the colour of the thorium complexes with the various reagents]

**Fig. 2.—Effect of pH on the colour of the thorium complexes with the various reagents:**
1. Arsenazo I, conc. Th-1-2 \(\times 10^{-4}\)M, 650 m\(\mu\);
2. Arsenazo II, conc. Th-1-2 \(\times 10^{-5}\)M, 600 m\(\mu\);
3. Arsenazo III, conc. Th-0-4 \(\times 10^{-5}\)M, 665 m\(\mu\);
4. Arsenazo III, concentration of the reagents 0-5 \(\times 10^{-4}\)M.

**Uranium**

The method for the determination of quadrivalent uranium with arsenazo III is considerably more selective than for the determination of uranium\textsuperscript{IV}. Preliminary reduction has to be carried out; this and the stability of uranium\textsuperscript{IV} may cause various difficulties; however, this method of determining uranium appears to be most satisfactory.\textsuperscript{11} As in the case of thorium most cations and anions do not inhibit the reaction. Zirconium is masked by oxalic acid and iron\textsuperscript{III} is reduced with ascorbic acid. Only thorium causes substantial interference. The following analysis procedure may be used when the quantities of uranium and thorium are of the same order: up to the time of reduction of uranium only thorium is determined; after completion of the reduction the sum of thorium + uranium\textsuperscript{IV} is determined and the uranium content found from the difference.

The method of determination is as follows:\textsuperscript{11}

Decompose 0-5 g of the rock sample, ore cake, etc., containing 0-002% and larger quantities of uranium, by heating with hydrochloric acid + hydrogen peroxide. Dilute with 4N hydrochloric acid and filter into a 100-ml volumetric flask. Take two aliquots of 10 ml each and place in small flasks. Add 5–10 mg of ascorbic acid to both fractions (until discoloration of the brown colour of iron\textsuperscript{II} sets in) and to one fraction 5–6 granules of zinc (to reduce the uranium). Run off the solutions into 50-ml volumetric flasks, without transferring the zinc, and rinse out the flasks with 4N hydrochloric acid.

To each test sample add 2 ml of 4% oxalic acid solution, 2 ml of a 0-05% solution of arsenazo III and dilute to the mark with 4N hydrochloric acid. Photometric measurements are carried out at
680 m\textmu{} or on a photocolorimeter with a red-light filter in 20-mm cells, using the non-reduced aliquot as a standard.

The uranium content is found via a calibration curve: small volumes of the solution, containing, respectively 0, 4, 8, 15, 30 and 40 \textmu{}g of uranium are subjected to the above procedures whilst maintaining accurately the degree of acidity, the period of reduction and other conditions.

The extraction-photometric method\textsuperscript{7} can be used to achieve improved selectivity during the determination of hexavalent uranium.

Decompose a few mg of the sample, containing 1-50 \textmu{}g of uranium, according to the mineralogical composition of the sample. After evaporation, treat the dry residue with 2.0 ml of 0.05N hydrochloric acid, 2.5 ml of a 5\% solution of Trilon B, 1.00 ml of a 0.05 \% solution of arsenazo III, 0.5 ml of a 20\% solution of diphenylguanidine chloride and add 5.00 ml of butanol. After extraction, transfer part of the upper layer to a 10-mm cell and evaluate photometrically, either on a spectrophotometer at 660 m\textmu{} or on a photocolorimeter with a red-light filter.

The uranium content is found via a calibration curve plotted in the manner described above.

Direct photometric determination without separation of the stable elements can be employed when determining uranium in pitchblende or in substances containing traces of admixtures. Sulphates, phosphates and even limited quantities of fluorides do not act as inhibitors. The photometric determination of uranyl ion is carried out at pH 1.5-3.5, and of uranium\textsuperscript{IV} in 3-9N hydrochloric acid.

Zirconium

The method is very selective for the determination of zirconium. In most cases, even during the determination of zirconium in complex samples, \textit{e.g.} in ores,\textsuperscript{12} and alloys based on copper, aluminium, magnesium and titanium, in the presence of niobium, tantalum and other elements,\textsuperscript{13} it is not necessary to separate the stable elements or to concentrate the zirconium. Photometric measurements can be taken immediately after decomposing the sample. The complex of arsenazo III and zirconium is very stable and sulphates, phosphates and other anions have only a slight effect. Oxalates and fluorides mask zirconium. The sensitivity is approximately 0.01-0.05 \textmu{}g/ml of zirconium (see Table II).

The effect of the acidity and the ratio of zirconium: arsenazo III on the intensity of coloration is shown in Figs. 3 and 4. The determination of zirconium can be carried out in strongly acidic media—from 2 to 11N hydrochloric acid \textit{i.e.} under conditions where practically no hydrolysis or partial polymerisation of the zirconium cations occurs. This ensures very accurate results and good reproducibility of the analyses.

Goryushina and Romanova\textsuperscript{12} showed that even in such complex samples as tin and titanium concentrates, magnesium fractions obtained on concentrating ores of various origin, \textit{etc.}, direct photometric determination of zirconium can be carried out in solutions obtained after decomposing the substances, without preliminary separation of the stable elements:\textsuperscript{12}

Fuse 0.1-0.2 g of the material in a platinum dish with 5 g of a mixture (1:1.5) of borax and sodium carbonate at 900\textdegree{}, for 7 to 10 min. After cooling, add boiling water and decant the liquid, with the residue of hydrates, into a beaker. Dilute the mixture with water to 150 ml and heat to achieve better coagulation. Filter off the residue, wash and dissolve in 2N hydrochloric acid. Aliquots containing 5 to 30 \textmu{}g of zirconium are taken; to these are added 3 ml of a 1\% gelatin solution, 1.00 ml of a 0.1 \% solution of arsenazo III and up to 50.0 ml of 2N hydrochloric acid. Photometric measurements are taken with a FFK-M, in a 2.0-cm cell, with a red-light filter. The zirconium-content is found via a calibration curve, plotted under identical conditions.
Analytical use of arsenazo III

The concentration of 2N hydrochloric acid was selected on considering the most practical working conditions for the analysis of substances containing high or average concentrations of zirconium (0.1% or more of zirconium). When the zirconium-content is low (0.01% and less) determinations should be carried out in 9N hydrochloric acid. The only drawback is the relatively high volatility of hydrochloric acid. In some cases it may be more advantageous to work at acidities corresponding to the azeotropic composition of the system—hydrochloric acid 1:1 (~6.1N hydrochloric acid).14

Zirconium must be concentrated when analysing alloys and substances containing zirconium in the form of admixtures (from 0.01% to 0.0001%). Titanium is known to be a very good co-precipitator for zirconium but its use has been proved inadvisable because it causes considerable interference when determining zirconium photometrically with reagents such as pyrocatechol violet, morin, phenylfluorone etc. These difficulties do not arise with arsenazo III. Titanium causes no interference even at ratios of zirconium:titanium = 1:1000. The determination of zirconium in aluminium-magnesium alloys is described as an example; it was investigated by Kuznetsov and the present author:

![Graph](image-url)

Fig. 3.—Effect of the concentration of hydrochloric acid and of the molar ratio of zirconium:reagent on the colour intensity (Concentration of arsenazo III: 0.9 x 10^{-3} M, spectrophotometer SF-4, 665 μm, 10-mm cell).
Weighed samples of the alloy (0.2–2 g), supposedly containing 2–40 µg of zirconium, are dissolved in 6N hydrochloric acid, to which nitric acid is added—to dissolve the copper.

Evaporate the samples to wet salts* and add 1 ml of a titanium solution containing 5 mg/ml of titanium, 5 ml 6N hydrochloric acid, then dilute with water to 50–100 ml.

Add 13 ml of 40% sodium acetate trihydrate solution. Check the acidity with universal indicator paper; the pH should be within the limits 2.0 to 2.5.

Maintain on a hot water bath for 30–60 min. The small quantity of flaky precipitate of titanium and zirconium hydroxides is filtered through a 7-cm diameter filter paper and washed with water.

Transfer the filter, together with the residue, into the same beaker in which the precipitation was carried out, add 10 ml of 6N hydrochloric acid and heat the mixture for 15–20 min whilst stirring with a small glass rod. A homogeneous paper pulp is formed and the solution is filtered into a 50-ml volumetric flask; the beaker and filter are washed 3 times with small quantities (2-5 to 3 ml) of 6N hydrochloric acid. It is necessary to allow the solution to drain off completely after each washing because the volume of 6N hydrochloric acid, which can be used for the washing is limited to 9–10 ml.

Add 1.00 ml of an arsenazo III solution, agitate the mixture, then add 30.0 ml of conc. hydrochloric acid (sp. gr. 1.18†) and dilute with 6N hydrochloric acid to the mark. Close the flask tightly to avoid losses in hydrochloric acid.

* Evaporation to wet salts is not absolutely necessary. In this case the required pH of the solution is established, after diluting the solution, by using universal indicator paper or an internal indicator e.g. methyl violet, adding sodium acetate until the colour changes from blue to dark blue-violet.

† Use 28 ml when the sp. gr. of the conc. hydrochloric acid is 1.19, 32 ml for a sp. gr. of 1.17 and 34 ml for a sp. gr. of 1.16.
Photometric measurements are carried out on a spectrophotometer at 665 m\,\mu\text{m}, in a 10-mm cell, or on a photocolorimeter with a red-light filter, in a 20-mm cell. The solution of the No. 1 calibration curve is used as standard.

**Calibration curve.** Introduce into a series of 50-ml volumetric flasks: 0, 0.4, 0.8, 1.6, 4.0, 6.0 and 8.0 ml, respectively, of a zirconium solution in 6\,N hydrochloric acid containing 5 \mu\text{g}/ml of zirconium, a titanium solution in 6\,N hydrochloric acid, containing 5 mg/ml of titanium, 1.0 ml; a 0.25 % solution of arsenazo III, 1.00 ml; conc. hydrochloric acid, 30 ml (sp. gr. 1.18); and dilute with 6\,N hydrochloric acid to the mark.

**Note.** Instead of 6\,N hydrochloric acid, azeotropic hydrochloric acid (\sim 6.1\,N hydrochloric acid) can be used, or a 1:1 solution of hydrochloric acid prepared from the conc. acid. In this case the calibration curve is plotted using the 1:1 acid.

**Zirconium and hafnium**

Arsenazo III can also be used for the photometric determination of zirconium and hafnium when both elements are present. The principle of the method has been described earlier and is general for all reagents giving colour reactions with zirconium and hafnium. It is as follows: the sum of zirconium + hafnium is determined photometrically at two pH values at which superposition is observed in the first case and at which, in the second case, the largest discrepancy occurs between the colour intensity of the corresponding zirconium and hafnium complexes. The zirconium and hafnium contents can be calculated from the results obtained. Elinston and Mirzoyan state that the photometric determination of zirconium + hafnium should be carried out in 1\,N and 4\,N hydrochloric acid.

**Rare earths**

In weakly acidic solutions yttrium, lanthanum and the lanthanides develop a blue-green coloration with arsenazo III. Scandium gives a violet colour. The determination is of a sufficiently high degree of sensitivity: 0.5 \mu\text{g} of the element and larger quantities can be determined in 25 ml of solution. The reaction is not very selective: all elements reacting with arsenazo III act as inhibitors when the pH at which they begin to hydrolyse is lower than the pH of the start of the hydrolysis of the rare earth elements. The following substances do not act as inhibitors in quantities up to 5–50 mg in 25 ml: aluminium, iron, magnesium, sodium, potassium, sulphates, chlorides, phosphates.

**Analogues of arsenazo III**

Kuznetsov, Dedkov and Savvin succeeded in synthesising completely different analogues of arsenazo III by the azo-addition of arsenazo I and various amines on adding calcium salts:

\[
\begin{align*}
\text{AsO}_2\text{H}_2 & \quad \text{HO}_3\text{S} \\
\text{OH} & \quad \text{OH} \\
\text{N=N} & \quad \text{X} \\
\text{YO} & \quad \text{Y} \\
\text{Nimetals} & \quad \text{SO}_3\text{H}
\end{align*}
\]

where \(X = H; Y = \text{H}_2\text{SO}_4\text{H}, \text{NH}_2\text{NO}_3, \text{N(CH}_3)_2, \text{A}_3\text{O}_3\text{H}_2;\)

\(Y = H; X = \text{COOH}, \text{SO}_3\text{H}, \text{OH}, \text{NO}_2.\)

Preliminary analytical tests have proved that these compounds also give colour reactions with many elements, especially with those where arsenazo I and arsenazo III
give colour reactions. The stability of complexes formed by these compounds lies between the stability of the corresponding complexes of arsenazo I and arsenazo III. Further investigations will be carried out on the bis-azo-derivatives of chromotropic acid.

**Synthesis of arsenazo III**

The synthesis is quite simple and easily reproducible.

The compound is prepared by the azo-addition of concentrated solutions of diazotised o-aminophenylarsonic acid and chromotropic acid in a medium of excess calcium hydroxide which is used simultaneously as a base and as an activator.

Dissolve 15 g (0.069 mole) of o-aminophenylarsonic acid, whilst heating slightly, in 30 ml of water and 15 ml of conc. hydrochloric acid (sp. gr. 1.18). After cooling, add 50 g of crushed ice. To this mixture add, with constant stirring, a solution of 5 g of sodium nitrite in 10–15 ml of water and a small excess of nitric acid (accurately tested with iodised starch paper) which is subsequently removed with sulphamic acid.

Dissolve 6.5 g (0.0179 mole) of the disodium salt of chromotropic acid in 20 ml of water and introduce a mixture of 10 g of calcium oxide and 30 ml of water into the solution. Add 50 g of crushed ice as well as the previously prepared diazonium solution, under constant agitation. The solution turns a blue-violet colour. Allow to stand for 30 min to 2 hr at room temperature.

Carry out tests to ascertain the termination of the azo-addition reaction. Add 1 drop of the reaction mixture (ca. 0.03 ml) to 50–100 ml of water. Place 5–10 ml of the resulting blue solution in a test tube and to this add 2–3 drops of conc. hydrochloric acid. The solution turns pinkish-crimson. Add 1 drop of thorium salt solution, containing 10–20 mg/ml of thorium, when the solution acquires the intensive emerald-green colour of the thorium-arsenazo III complex. Decant the solution into two test tubes and to one test tube add 10–15 drops (ca. 0.5 ml) of conc. sulphuric acid, whilst constantly agitating and cooling the contents of the test tube. The colour of the solution to which conc. sulphuric acid has been added will differ slightly from the colour of the second fraction if complete addition has occurred; it will turn dark green. If, on the other hand, incomplete addition took place, then the fraction containing sulphuric acid will turn red-violet, crimson or acquire a muddy colour; in this case a mixture of arsenazo I and arsenazo III has been obtained. This may be caused by inadequate purity of the starting materials, i.e. of the chromotropic acid and especially of o-aminophenylarsonic acid.

Add 1 litre of hot water and 100 ml of conc. hydrochloric acid to the mixture obtained by the addition reaction. Agitate the mixture to dissolve the calcium salts completely, and filter after allowing to settle. Wash the almost black residue with 50–100 ml of hydrochloric acid (1:10) and discard the filtrate. Dissolve the crude product in 1 litre of hot water + 50 ml of 40% sodium hydroxide solution, freed from mechanical admixtures by filtration, acidity with 100 ml of conc. hydrochloric acid and allow to stand for a few hr or overnight. Filter off the precipitate, centrifuge and wash it first with 30–50 ml of water, then with 30–50 ml of ethanol. The last fractions of the filtrate should be free from reaction by-products, i.e. from arsenazo I and decomposition products of the excess diazonium compound of o-aminophenylarsonic acid. This is tested by the above described qualitative reaction with thorium salts. The yield of arsenazo III is 11–12 g.


**Résumé**—Le réactif arsenazo III (1,8-dihydroxynaphthalène-3,6-disulfonylique acide-2,7-bis[azo-2-phénylarsonique acide]) donne des réactions colorées avec un certain nombre d'éléments. Les anions n'influent que très peu sur les réactions, et il est possible de travailler à de faibles valeurs de pH. La
réaction est très sensible, le composé peut ensuite être utilisé pour le dosage photométrique de Th, Zr, Hf, U et d'autres éléments. La méthode est la plus sélective pour Th, Zr et U(IV). Les matériaux contenant ces éléments peuvent être analysés directement, dans des solutions formées après dissolution des échantillons, sans séparation des éléments.

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