Extraction Preconcentration of Vanadium(V) as a Complex with 2-Hydroxy-5-\(t\)-Butylphenol-4'-Methoxyazobenzene and Its Determination by Atomic Absorption Spectrometry

A. M. Pashadzhanov
Institute of Chemical Problems, Academy of Sciences of Azerbaijan, pr. G. Dja vida 29, Baku, 370143 Azerbaijan

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Abstract—The complexation of vanadium(V) with 2-hydroxy-5-\(t\)-butylphenol-4'-methoxyazobenzene was studied. Optimum complexation conditions were found. The main spectrophotometric parameters of the resulting complexes were determined. A procedure was developed for determining vanadium in soils.

The synthesis and study of new organic reagents for shortening the time of element determination and improving the accuracy of analysis are current problems in spectrophotometry. In this aspect, nitrogen-containing azo compounds for the photometric determination of vanadium(V) are promising as reagents [1, 2]. It was found with 4-(2-pyridylazo)resorcinol as an example that the analytical potentials of this class of reagents in determining vanadium are significantly extended when aqueous–organic media are used [3, 4].

Preconcentration is used to lower the detection limit for vanadium in various samples.

Vanadium is most frequently preconcentrated by extracting its methyl isobutyl ketone complex with Cupferron (ammonium N-nitrosophenylhydroxylamine) or ammonium pyrrolidine dithiocarbamate [5]. We studied the complexation of vanadium with 2-hydroxy-5-\(t\)-butylphenol-4'-methoxyazobenzene and the conditions for the extraction preconcentration of vanadium and its determination in soils using atomic absorption spectrometry.

EXPERIMENTAL

Reagents and apparatus. A 1.5 \(\times\) 10\(^{-5}\) M stock solution of vanadium(V) in twice-distilled water was prepared from chemically pure ammonium vanadate. Working vanadium solutions were prepared by diluting the stock solution. A 3.5 \(\times\) 10\(^{-4}\) M solution of 2-hydroxy-5-\(t\)-butylphenol-4'-methoxyazobenzene was prepared by dissolving an exact portion of the reagent in ethanol.

2-Hydroxy-5-\(t\)-butylphenol-4'-methoxyazobenzene (HR) was synthesized by the procedure described in [6]. It is a monobasic acid,

\[
\begin{align*}
\text{C}_4\text{H}_9 & \quad \text{N} = \text{N} & \quad \text{OCH}_3 \\
\text{OH} & \\
\end{align*}
\]

The composition and structure of the reagent were determined by elemental analysis and IR and UV spectrometry. It is a brown crystal, soluble in methanol, ethanol, propanol, isopropanol, acetone, and other solvents.

The required pH values were adjusted using ammonium acetate (pH 3–10) and chloride (pH 1–2) buffer solutions; pH was controlled with an EV-74 universal potentiometer. The ionic strength of the solutions (0.1) was maintained with KCl. Benzene, toluene, chloroform, carbon tetrachloride, dichlorehane, butanol, and hexane were used as organic solvents.

The absorbance of extracts was measured on a KFK-2 photocolorimeter and an SF-46 spectrophotometer.

An AAS-1N atomic absorption spectrometer with a hollow-cathode lamp (Carl Zeiss Jena, Germany) was used. The optimum measurement conditions are given in Table 1.

<table>
<thead>
<tr>
<th>Wave-length (nm)</th>
<th>Lamp current (mA)</th>
<th>Slit (nm)</th>
<th>Acetylene flow rate (L/h)</th>
<th>Nitrogen monoxide flow rate (L/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>318.5</td>
<td>20</td>
<td>0.5</td>
<td>200</td>
<td>180</td>
</tr>
</tbody>
</table>

Procedure. A specified volume of the stock \(\text{NH}_4\text{VO}_3\) solution, several milliliters of a buffer solution of an appropriate pH, and corresponding volumes of a 2-hydroxy-5-\(t\)-butylphenol-4'-methoxyazobenzene...
solution were placed in graduated test tubes with
ground-glass stoppers. The mixtures were diluted with
the same buffer solution to a volume of 10 mL and
shaken with 5 mL of an organic solvent for 1 min. After
phase separation, the organic layer was isolated and its
absorbance or atomic absorption was measured under
optimum conditions.

RESULTS AND DISCUSSION

HR forms a colored complex with vanadium(V) in
the pH range 2–9. The optimum acidity for complex for-
mination and extraction corresponds to pH 4.5 (Fig. 1).

Chloroform, dichlorethane, carbon tetrachloride,
benzene, toluene, xylene, hexane, cyclohexane, and
butanol were used for extracting the complex. The best
extractant was chloroform (Table 2); it was used in the
further studies.

The equilibrium concentration of vanadium(V) in
the aqueous phase was determined by atomic absorp-
tion spectrometry.

The concentration of vanadium in the organic phase
was found as the difference. The single-step extraction
with chloroform recovered 98% of vanadium(V) as a
complex.

To reveal the effect of reagent concentration on the
complex formation, a series of experiments was con-
ducted using a constant concentration of vanadium and
variable concentrations of the reagent. The recovery of
vanadium increased when the HR concentration was
increased to $3.5 \times 10^{-4}$ M; the further increase in the
reagent concentration had no effect on the extraction of
vanadium.

The effect of the aqueous- and organic-phase vol-
umes and exposure time on the formation and recovery
of the vanadium(V) complex was studied. An increase
in the volume of the aqueous phase to 10 mL did not
reduce the absorbance of chloroform extracts. The
vanadium(V) complex formed immediately after mix-
ing the reagent solutions and was stable for two days.

Under optimum conditions, absorption maxima
were observed at 480–530 and 370 nm; the bathochromic
shift was 160 nm. The shape of the absorption spectrum
of the extract points to the formation of a single com-
plex.

The molar ratio of components in the complex was
determined by the Asmus straight-line technique and
the slope method [7] (Fig. 3).

In solution of pH 3.5–4.5, vanadium(V) occurs as
$\text{VO(OH)}^{2+}$. In the course of complexation, one proton
is displaced from each reagent molecule [8].

Table 2. Recovery ($R, \%$) of vanadium(V) complex with
organic solvents: $1.5 \times 10^{-5}$ M vanadium(V); pH 4.5

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$R, %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>71.0</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>70.0</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>85.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>94.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>89.1</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>75.1</td>
</tr>
<tr>
<td>Chloroform</td>
<td>98.0</td>
</tr>
<tr>
<td>Dichlorethane</td>
<td>92.0</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>75.0</td>
</tr>
</tbody>
</table>