Azo-Substitute of Ethoxy Acridine – A New Reagent for Extraction-
Photometric Determination of Tellurium (IV)

N.I. Ismayilov, A.M. Pashajanov, G.R. Muradova
M. Nagiyev Institute of Catalysis and Inorganic Chemistry of Azerbaijan National Academy of Sciences,
Department of Analytical Chemistry, AZ 1143, H. Javid Ave. 113, Baku, Azerbaijan
namig.ismayilov@yahoo.com

M. Nagiyev Institute of Catalysis and Inorganic Chemistry of Azerbaijan National Academy of Sciences,
Department of Analytical Chemistry, AZ 1143, H. Javid Ave. 113, Baku, Azerbaijan
aydin.pashajanov@gmail.com

M. Nagiyev Institute of Catalysis and Inorganic Chemistry of Azerbaijan National Academy of Sciences,
Department of Analytical Chemistry, AZ 1143, H. Javid Ave. 113, Baku, Azerbaijan

Abstract
We studied associates of halogen telluride (Cl, Br) with 9-amine-4-ethoxyacridine-6-azo-N,N-diethylaniline (AEADEA) by
spectrophotometric method. It was established that associates are extracted well with chloroform-acetone (3:2). We
determined the compositions, physical and chemical and analytical properties of complexes (\( \lambda_{\text{max}} \), D, R%). Maximum
light absorption for chloride complexes is found to be \( \lambda_{\text{max}} \approx 520 \) nm, but for bromide complexes \( \lambda_{\text{max}} \approx 530 \) nm. For
establishing the composition of azo-substitute of ethoxyacridine the synthesized reagents were exposed to elemental
analysis, as well titrimetric titration by azo group. We developed new extraction-photometric determination methods of
tellurium. Lambert-Beer law is observed in the range 0.5-15 mkg Te at 5 ml medium.

Indexing terms/Keywords
9-amine-4-ethoxyacridine-6-azo-diethylaniline; extraction-photometric determination of tellurium; halogen tellurate.

Academic Discipline And Sub-Disciplines
Chemistry

SUBJECT CLASSIFICATION
Analytical chemistry; Inorganic chemistry

TYPE (METHOD/APPRAOCH)
Spectrophotometry, extraction-photometric determination

INTRODUCTION
Only sulfur containing chelating reagents are used for photometric determination of tellurium which is characterized with
a high sulfur affinity. As a rule, the elements which have a high sulfur affinity and are often accompanied by tellurium impede
the determination: Ag, As, Au, Cu, Hg, Se, Ti and platinum metals. That’s why the preliminary separation of tellurium is
often necessary, for which the use of diethylthiocarbamate is relevant [1-2].

Methods of extraction-photometric determination of tellurium with basic dyestuffs are well known [3-4], among which
butylrhodamine C is often used. Butylrhodamine C is low-selective. Fe (III), Cu (I), Pb (II), Sn (II, IV), Ti (III), Sb (V), In (III),
Au (III), Ag (I) and Ga\(^{3+}\) interfere with the determination of tellurium. Results of determination are unrepeatable which force
to apply severe conditions of analysis.

When determining the metals with no chromophoric properties as ion-associates, their metal halogenide complexes with
cations of basic dyes, sensitivity of determination depends on intensity of reagent staining. Ethoxyacridine does not have a
large connectivity system and, consequently blue color. The detection limit of elements by this dyestuff is high [5-6]. This
defect can be eliminated by increasing conjugated chain due to formation of azo-substitute of ethoxyacridine.

In the present work we present the experimental results of associates of chloro-telluride and bromium telluride (HTeCl\(_2\),
HTeBr\(_2\)), with azoethoxyacridine-9-amine-4-ethoxyacridine-6-azo-N,N-diethylaniline (AEADEA), and possibility of using
them in photometric analysis was found out.

EXPERIMENTAL
Reagents and instruments
9.71 \times 10^{-3} \text{M} solution of tellurium (IV) was prepared from metal tellurium with high-purity (99.999%) by the method [7],
9.71 \times 10^{-3} \text{M} (22 mkg) solution of tellurium (IV) was obtained by diluting the initial solution. Solution AEADEA (0.05%) was
prepared by dissolving doublecrystallized preparation in ethanol. Acidity of medium was created with solution of
sulphuric acid (9.00 M), 1.00 M solution LiCl and 1.00 M KBr were used.
Spectrophotometric researches were conducted on spectrophotometer UB-1800 visible. While developing analytical formulas light absorption of painted extracts was measured on photoelectrocalorimeter KFK-2. pH value of solutions was determined by ionomer EB-74.

**Technique**

Various quantities of tellurium (IV) were placed into test-tubes with friction lid, necessary acidity of sulphuric acid was created, 0.5 ml solution LiCl (KBr), 0.5 ml solution AEADEA were added, and the volume of mixture was brought to 5 ml with water. The mixture was slightly shaken to mix the components; 5 ml extractant (chloroform-acetone 3:2) was added into it. Then, we separated organic phase from water phase, measured light absorption of extracts relative to reference solution.

**RESULTS AND DISCUSSION**

Application of sulphuric acid allows us to vary acidity of medium in wider interval. It was established that in the interval 1-10 N acidity of medium basic azo-dye exists in orange color in the form of unprotonated single charged cation \( R^+ \) with \( \lambda_{\text{max}} \) 460 nm. In the interval 10-16 N reagent is in monoprotonated form: a new absorption band with two maxima appears from 16 to 33 N on curves of light absorption at \( \lambda_{\text{max}} \) 380 nm and \( \lambda_{\text{max}} \) 580-590 nm, which is related to the addition to dye molecule of the second proton \( H^+ \)…\( R^+ \)…\( H^+ \)… This form was painted violet.

Thus, protonization of azo substitutes of ethoxyacridine can be represented with a scheme:

\[
R^+ + \overset{H^+}{\underset{\text{HO}^-}{\leftrightarrow}} R^+ ... H^+ + \overset{H^+}{\underset{\text{HO}^-}{\leftrightarrow}} H^+ ... R^+ ... H^+ 
\]

Condition of AEADEA in the interval 1-33 N by sulphuric acid was studied by spectrophotometric method (fig. 1).

Fig. 1: Absorption band of AEADEA at different acidities of solution: 1-1N, 2-9 N, 3-15 N, 4-29 N, 5-33 N by sulphuric acid (SF-46, 1=1 cm, [C\text{AEADEA}] = 4.18 \times 10^{-4} M).

Ethoxyacridine dyes were synthesized in the laboratory of analytical chemistry of the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiyev of NAS of Azerbaijan. Individuality of reagents was established by elemental analysis, titrometric titration by azo-group.

**Elemental analysis of ethoxyacridine dye.**

To establish the composition of azo-substitutes of ethoxyacridine synthesized reagents were exposed to elemental analysis. First, the preparation was dried 2-3 hrs at 50°C in vacuum oven to eliminate humidity. Results of analysis are given in the table 1.

| Compound | Theoretically calculated | Practically found |
|----------|--------------------------|-------------------|
|          | Total content of components, % |                      |
|          | C  | N  | H  | Cl | C  | N  | H  | Cl |
| AEADE    | 66.89 | 15.60 | 6.02 | 7.92 | 66.10 | 14.47 | 6.47 | 8.04 |
The formation and extraction of associates of chloride and bromide acid-complexes Te(IV) with AEADE were studied. Peaks of light absorption of chloride and bromide associates of tellurium (IV) with AEADE are observed in the interval 520-530 nm (fig. 2.)

Light absorption of extracts of associates is the same as the peak of ethoxyacridine which indicates electrostatic character of interaction and formation of complexes. During formation and extraction of complexes optimum acidity is in the interval 2.0-4.0 N by H₂SO₄. Under these conditions reagents are insignificantly extracted.

Organic solvents of various types: hydrocarbons, alcohols, simple and complex ethers, ketons, halogen derivatives of hydrocarbons were tested as extractants. It turned out that hydrocarbons (hexane, xylol, benzene) do not extract associates; simple salts of dyes, alcohols and halogen derivatives of hydrocarbons insignificantly extract associates, but ketons extract both associates and dyes. That’s why we studied organic solvents as extractants which were taken in different combinations; the best extractant is found to be the mixture of chloroform-acetone (3:2).

Optimum volume of water and organic phase equals to 5 ml. Molar ratio of components in extractable compounds was studied by methods of isomolar series, shift of equilibrium and straight line [8]. It was found that halogenide associates of tellurium (IV) are associated with AEADE in the ratio 1:1.

Based on the established ratio of components in extractable compounds we calculated the extraction constants by limiting logarithmic method of Asmus [8].

**Table 2. Physical and chemical characteristics of halogen tellurites with AEADE**

| Associate         | Optimum acidity of medium, N | λmax, nm | εx10⁻⁴ | βKD10⁻⁵ | D     | R, %  | Ratio Te:hal.:R⁺ |
|-------------------|------------------------------|---------|---------|---------|-------|------|-----------------|
| [HTeCl₆⁶] · AEADE | 3.0                          | 520     | 6.20    | 4.70    | 105.8 | 98.64| 1:6:1           |
| [HTeBr₆⁶] · AEADE | 4.0                          | 530     | 6.80    | 5.90    | 125.25| 98.80| 1:6:1           |

**The execution of definition**

0.5-15.0 mkg of tellurium (IV) was placed into test-tubes with friction lid, and 0.4 ml 1.0 M KBr, 1.6 ml 9 M H₂SO₄ were added. 0.5 ml of 0.1 alcohol solvent AEADEA was added into the mixture, the volume of mixture was brought to 5 ml with distilled water and light absorption of extracts were measured in the cell with 0.5 cm at 490 nm wavelength on KFK-2. Lambert-Beer law is observed in the range 0.5-15 mkg Te at 5 ml medium.

The followings do not interfere with the determination of tellurium: large amount of alkali and alkaline-earth metals Co(II), Co(III), Ni(II), Al³⁺, Cu(I), Cu(II), Ti(II), Pb(II), Sn(II), Fe(II), Ta(V), Nb(V), as well as anions PO₄³⁻, NO₃⁻, SO₄²⁻, C₂O₄²⁻, tartrate-
ion, citrate-ion, EDTA. Au(III), Fe(III), Se(IV), Ti(III), Hg(II), In(III), as well as thiocarbamide interfere with the determination of tellurium.

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Author' biography with Photo

Dr. Namig Ismayil Ismayilov works in the laboratory “Analytical Chemistry” in M.Nagiyev Institute of Catalysis and Inorganic Chemistry of Azerbaijan National Academy of Sciences. His scientific direction: development of new extraction-photometric determination methods of Ga, Te, In, Au, Hg and others. He is the author of more than 45 scientific works, including one patent.