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Abstract

Full Text

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Study of Organic Derivatives of Selenious and Tellurous Acids as Analytical Reagents

Up to the present time, investigators have devoted much attention to the study of organic reagents containing the atomic groupings: –COOH, –OH, =NOH, –SH, $-NH_2$, etc. Considerably less study has been made of organic compounds containing groups that include arsenic, sulfur, and especially phosphorus.

Meanwhile, organic reagents containing the groups $-AsO_3H_2$, $-PO_3H_2$ are of very great interest from the analytical point of view, as has been shown in a number of works ([1]-[12]).

Organic compounds containing the groups $-SeO_2H$, $-SeO_3H$, $-TeO_2H$, $-TeO_3H$ have not yet been studied with the aim of using them for quantitative analysis. From the literature data there is known only a brief indication by Feigl ([2]) that benzeneseleninic acid forms sparingly soluble precipitates with tetravalent elements and that these reagents may be used for analysis. Feigl also notes that, among reagents containing a sulfinic or seleninic group, only those in which the acid residue is directly attached to the aromatic nucleus are capable of precipitating tetravalent metals,

$$C_6H_5SO_2H, \qquad C_6H_5SeO_2H$$

whereas the presence of a CH_2 group,

$$C_6H_5CH_2SO_2H, \qquad C_6H_5CH_2SeO_2H$$

prevents precipitation.

This assertion proved to be incorrect. Both types of reagents are capable of precipitating from acid solutions the ions listed below; the difference consists only in the somewhat greater solubility of compounds containing the CH_2 group (see Table 3).

Feigl also considers that benzenesulfinic acid is capable of tautomeric transformation ([1],[13])

$$\underset{(I)}{R{-}S(=O){-}OH} \rightleftharpoons \underset{(II)}{R{-}S(=O)(H){=}O},$$

and, proceeding from these ideas, he assigns the following structure to the compound formed:

$$\begin{array}{c} \mathrm{O} \\ \| \\ \mathrm{C_6H_4{-}S{=}O} \\ \cdots \mathrm{Me^{+n}/n} \end{array} \qquad (\mathrm{Me} = \mathrm{Ti^{+4},\ Zr^{+4},\ Th^{+4}}).$$

However, our investigation showed that it is the first form that reacts, and the compounds formed are typical salts of the corresponding acids, insoluble in organic solvents (ethyl ether, chloroform, etc.).

Feigl' s conclusions concerning the ability of cerium(IV) in acidic solution to form precipitates with benzenesulfinic acid also proved to be incorrect. In fact, as we established, when cerium(IV) interacts with benzenesulfinic acid, an oxidation–reduction reaction takes place, as a result of which cerium(IV) is reduced to cerium(III), while benzenesulfinic acid ($R—SO_2H$) is oxidized to benzenesulfonic acid ($R—SO_3H$) and, in addition, disulfone $(RSO_2)_2$ is formed—a white flocculent precipitate. Cerium in the trivalent form remains quantitatively in solution.

A similar precipitate is also formed under the action of other strong oxidizing agents.

Benzeneseleninic acid is less prone to oxidation, and therefore it forms a precipitate with cerium(IV).

We synthesized and, for the first time, examined a class of organic derivatives of selenious acid containing the functional analytical group $—SeO_2H$: methyl-, ethyl-, propyl-, butyl-, benzene- and naphthaleneseleninic acids, as well as a series of organic derivatives of selenious acid containing various substituents: *o*-nitro-, *p*-nitro-, *o*-carboxy-, *p*-methylbenzeneseleninic acids, etc.

In addition, benzylsulfinic, benzylseleninic, and benzenetellurinic acids were synthesized and examined.

Organic compounds of this type, owing to the presence of an inorganic acid residue—$—SeO_2H$ or $—TeO_2H$—react in neutral or weakly acidic solutions with many elements (see Table 1), forming sparingly soluble compounds.

Table 1

Results of qualitative reactions of organic derivatives of selenious and tellurous acids with inorganic ions in neutral or weakly acidic medium*

Reagent	Cu(II)	Ag	Be	Ba	La	Al	Tl	Zr	Th	Ce(IV)	Hf	Sn(IV)	Pb	Nb	Ta	Bi	Fe(III)	Co	Ni
$C_2H_5—SeONH_4$	—	—	—	—	—	—	+	+	+	+	+	+	+	+	+	+	+	—	—
$C_4H_9—SeO_2NH_4$	—	—	—	—	—	—	+	+	+	+	+	+	+	+	+	+	+	—	—

Reagent	Cu(II)	Ag	Be	Ba	La	Al	Tl	Zr	Th	Ce(IV)	Hf	Sn(IV)	Pb	Nb	Ta	Bi	Fe(III)	Co	Ni
C_6H_5—SeO_2NH_4					–	–	+	+	+	+	+	+	+	+	+	+	+	–	–
$C_{10}H_7$—SeO_2NH_4					–	–	+	+	+	+	+	+	+	+	+	+	+	+	–
O_2N—C_6H_4—SeO_2NH_4						–	+	+	+	+	+	+	+	+	+	+	+	–	–
H_3C—C_6H_4—SeO_2NH_4						–	+	+	+	+	+	+	+	+	+	+	+	+	–
C_6H_5—CH_2—SeO_2NH_4						–	+	+	+	+	+	+	+	+	+	+	+	–	–
C_6H_5—TeO_2NH_4					–	–	+	+	+	+	+	+	+	+	+	+	+	–	–
C_6H_5—SeO_3NH_4					–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
C_6H_5—TeO_3NH_4					–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

Note. The sign + denotes formation of a precipitate, – its absence.

* This table shows the possibility of a number of determinations and separations of elements, which will be reported in our other works. Copper, silver, lead, and cobalt are precipitated by a large excess of reagent.

On the contrary, the metallic salts of aromatic selenic acids (R—SeO_3H) and of the analogous telluric acids (R—TeO_3H) are readily soluble in water; therefore benzeneselenonic and benzenetelluronic acids cannot have such broad application in analysis.

Table 2

Dependence of the sensitivity of reactions for the detection of various ions on the molecular weight of the reagent

Reagent	Molecular weight	Fe(III)	Bi	Ti	Zr
$(NH_4)_2SeO_3$	163	10.1	9.4	4.4	3.3
C_3H_7—SeO_2NH_4	172	7.8	–	–	–
C_6H_5—SeO_2NH_4	206	2.7	2.6	1.3	1.0
$C_{10}H_7$—SeO_2NH_4	256	1.5	1.4	1.0	0.7

Of the synthesized group of reagents, the aromatic derivatives of selenous acid—benzene- and naphthaleneseleninic acids—are of greatest interest for analytical purposes, since they quantitatively precipitate from acidic solutions tetravalent elements—titanium, zirconium, hafnium, thorium, cerium, tin—as well as niobium, tantalum, bismuth, and iron(III).

The selectivity of the action of benzene- and naphthaleneseleninic acids can be increased by regulating pH and by using complexing agents.

Table 3

Solubility in water of iron and zirconium benzeneseleninates

Compound	Solubility, mol/l
$Fe(o\text{-}NO_2C_6H_4SeO_2)_3$	$4.4 \cdot 10^{-7}$
$Fe(C_6H_5CH_2SeO_2)_3$	$5.6 \cdot 10^{-7}$
$Fe(C_6H_5SeO_2)_3$	$4.0 \cdot 10^{-7}$
$Fe(p\text{-}CH_3C_6H_4SeO_2)_3$	$3.4 \cdot 10^{-7}$
$ZrO(o\text{-}NO_2C_6H_4SeO_2)_2$	$1.4 \cdot 10^{-7}$
$ZrO(C_6H_5SeO_2)_2$	$1.2 \cdot 10^{-7}$
$ZrO(p\text{-}CH_3C_6H_4SeO_2)_2$	$9.8 \cdot 10^{-8}$

The investigation showed that from strongly acidic solutions, for example in $2.0\,n$ HNO_3, zirconium is quantitatively precipitated by ammonium benzene- and naphthaleneseleninate. Most other elements are not precipitated and do not interfere with the determination of zirconium, with the exception of tin(IV), titanium, niobium, tantalum, and tetravalent cerium, which form analogous precipitates in strongly acidic solution.

The influence of the last four elements can easily be eliminated by adding hydrogen peroxide, which forms complex compounds with them and prevents their precipitation (in an acidic medium cerium is reduced by hydrogen peroxide to the trivalent state, and the latter does not form insoluble compounds with ammonium benzene- or naphthaleneseleninate). Tin(IV) must be removed beforehand by precipitation with hydrogen sulfide.

Table 3 gives the results for the solubility of certain compounds, obtained using radioactive isotopes of iron (59) and zirconium (95) as indicators.

The composition of the compounds listed was established on the basis of chemical-analysis data for the dried precipitates.

It should be noted that in the practice of analytical chemistry selenous acid has long been used for the separation and determination of zirconium ([13,14]), titanium ([15]), bismuth ([15]), niobium, tantalum, and zirconium ([16]), and also tellurous acid for the determination of bismuth ([17]), etc.

However, organic derivatives of these acids are more valuable analytical reagents, since they possess greater sensitiv-

···by the sensitivity and selectivity of action, especially when masking complex-forming reagents are used simultaneously.

We have developed new gravimetric and physicochemical methods for the determination of tetravalent elements—titanium, zirconium, etc., as well as bismuth and iron(III), in the presence of other elements, in industrial and natural objects, using ammonium benzene- and naphthaleneseleninates (Tables 4 and 5).

Table 4

Results of the potentiometric (a) and amperometric (b) determination of bismuth

Taken Bi, mg	Found Bi, mg	Found Bi, mg
	a	b
16.90	16.92	–
16.90	16.93	–
8.45	8.44	–
8.45	8.45	–
4.23	4.23	4.23
4.23	4.24	4.22
2.12	–	2.10
2.12	–	2.13

Table 5

Results of the determination of zirconium in eudialyte and of titanium in titanomagnetite by benzene- (a) and naphthaleneseleninate (b), phenylarsonate (c), and cupferronate methods (d)

Element	Found MeO_2	Found MeO_2	Found MeO_2	Found MeO_2
	a	b	c	d
ZrO_2	10.33	10.40	10.31	–
ZrO_2	10.30	10.28	10.36	–
TiO_2	41.83	41.97	–	41.86
TiO_2	41.74	41.69	–	41.90

The principle of the potentiometric and amperometric methods of determination is based on precipitation of the element with benzeneseleninic acid, followed by dissolution of the precipitate in a mineral acid and iodometric titration of the benzeneseleninic acid

$$Bi(NO_3)_3 + 3C_6H_5SeO_2H = Bi(C_6H_5SeO_2)_3 + 3HNO_3$$

$$2C_6H_5SeO_2H + 6KJ + 6HNO_3 = (C_6H_5Se)_2 + 3J_2 + 6KNO_3 + 4H_2O$$

$$Bi \equiv 9J \equiv 9Na_2S_2O_3$$

In conclusion, the possibility should be noted of radiometric titration using radioisotopes of the elements being determined or organic reagents containing radioisotopes of selenium or tellurium.

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Note: Figure translations are in progress. See original paper for figures.