

from 0.9 cm³ solution with an initial DNA concentration of 0.5γ cm⁻³ within <10 min.

Translated from *Zhurnal Neorganicheskoi Khimii*, 25, 567-569 (1980)

U.D.C. 546.244'226.04

DISCUSSION

The freshly prepared solid phase of HAP with ratio Ca/P = 1.58 is amorphous HAP according to the results of X-ray diffraction and infrared spectroscopy. This agrees with Termine and Eanes' results⁴, although they term such a composition "pseudohydroxyapatite". Conversion into the crystalline state has taken place after ageing for ~6 h and a stoichiometric composition is realised owing to the absorption of residual calcium from the mother-liquor. Such a prolonged change into the crystalline state of a substance in which the nature of the Ca²⁺-PO₄³⁻-OH⁻ bonds is retained unchanged (according to the infrared spectroscopic results) suggests mutual ordering of the primary microelements of the HAP structure and their unification into crystals which is accompanied by "healing" of the contact with the aid of calcium ions.

From an analysis of the published information on the production of HAP it seems that the phase composition of the material obtained is determined by the state of the phosphate ions in the initial solutions. Therefore under our conditions for the synthesis of HAP the initial solution of K₃PO₄ contains a high concentration of OH⁻ ions, which hinder the formation of phosphate hydrates and accordingly of foreign phases. The stoichiometric ratio of the components on mixing determines the production of a solid phase with the HAP structure.

From the results of Main and coworkers⁸, the size and form of the HAP crystals obtainable by the method described above are the best ones for the column chromatography of biopolymers. These crystals can be used as sorbents in medical biological investigations.

Tellurium(IV) Sulphato-complexes in Solution

B.I.Nabivanets, E.N.Oganesyan, E.E.Kapantsyan, and G.G.Babayan

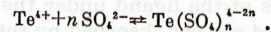
The stepwise stability constants of the tellurium sulphato-complexes have been determined by ion exchange: β₁ = 6.5 × 10²; β₂ = 3.6 × 10²; β₃ = 2.0 × 10² (t = 22 °C; I ≥ 3).

The main source of tellurium is the anode muds obtained in the sulphuric acid treatment of sulphide ores. In almost all the technological schemes the tellurium is converted into a soluble state, and in every instance hydrochloric or sulphuric acid in the presence of various oxidants is taken as solvent¹. Despite this, the state of the tellurium in sulphuric acid media has been little studied.

The aim of the present work was to determine the composition and stability constants of the tellurium sulphato-complexes formed in sulphuric acid solutions. For this, we studied the sorption of tellurium(IV) on KU-2† (H⁺ form) cation-exchange and AV-17# (SO₄²⁻ form) anion-exchange resins under static conditions at Σ{[H₂SO₄] + [HClO₄]} ≥ 3 M and ionic strength I ≥ 3. At sulphuric acid concentrations >3 M the ionic strength was not kept constant.

The experiments were carried out at an initial tellurium concentration of 2 × 10⁻⁴ g-ion litre⁻¹ (to avoid the formation of polymeric species² in the solution); the tellurium in the equilibrium solutions was determined photometrically with tin(II) chloride³. The experiments were carried out at 22 °C.

The results of the experiments on the absorption of tellurium by cation-exchange and anion-exchange resins are given in the Table. Preliminary calculations showed that several complexes are formed in the test system. On taking into account that at [H⁺] ≥ 3 N tellurium is found in the solution mainly as Te⁴⁺ cations², the formation of the sulphato-complexes can be represented by the equation



The Table shows that as the H₂SO₄ concentration is raised the absorption on the anion-exchange resin increases and remains almost constant in the range 4.5-5 M H₂SO₄. At such acidities it seems that the complex with the highest charged anion is formed. The charge of the complex was determined by a dynamic method by studying the total exchange capacity of the anion-exchange resin for the test ion and a standard ion with a known charge (Cl⁻). 0.1 N HCl was passed through a column containing 3 g AV-17 anion-exchange resin in SO₄²⁻ form. The total exchange capacity for Cl⁻ was 5.50 mg.equiv.g⁻¹. Then a sulphuric acid solution (4.5 M H₂SO₄)

† KU-2 is a monofunctional, strongly acid cation-exchange resin with -SO₃H active groups, prepared by treating a swollen styrene-divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

AV-17 is a strongly basic anion-exchange resin containing quaternary nitrogen-groups. It is based on styrene and trimethylamine (Ed. of Translation).

REFERENCES

1. E.M.Southern, *J.Mol.Biol.*, **94**, 51 (1975).
2. T.Kawasaki, *J.Chromatogr.*, **93**, 275 (1974).
3. A.L.Boskey and A.S.Posner, *J.Phys.Chem.*, **77**, 2313 (1973).
4. J.D.Terminé and E.D.Eanes, *Calc.Tiss.Res.*, **10**, 171 (1972).
5. A.L.Boskey and A.S.Posner, *J.Phys.Chem.*, **80**, 40 (1976).
6. L.S.Bell, A.M.Posner, and J.P.Quirk, *J.Coll.Interface Sci.*, **42**, 250 (1973).
7. A.N.Smith, A.M.Posner, and J.P.Quirk, *J.Coll. Interface Sci.*, **48**, 442 (1974).
8. R.K.Main, M.J.Wilkins, and L.J.Cole, *J.Amer.Chem. Soc.*, **81**, 6490 (1959).

of tellurium was passed through such a column until absorption of tellurium ceased; the total exchange capacity with respect to tellurium was 2.73 mmole g⁻¹. The charge was calculated by the formula:

$$Z = \frac{5.50}{2.73} = 2.01.$$

Experimental and calculated results for determining the stability constants of the tellurium sulphato-complexes.

$c_{\text{TeIV}} = 2 \times 10^{-4}$ g-atom litre⁻¹, $\Sigma\{[\text{HClO}_4] + [\text{H}_2\text{SO}_4]\} \geq 3 \text{ M}$.

Mass of ion-exchange resin taken = 1 g, volumes of solutions 20 ml.

[H ₂ SO ₄] _M	10 ³ [SO ₄ ²⁻]*	-lg [SO ₄ ²⁻]	Absorption, %		γ ₊	γ ₊₋₁	γ ₋	\bar{n}
			KU-2	AV-17				
0	0	--	45.0	0	1.00	0	0	0
0.16	0.264	3.578	41.5	7.0	0.91	-0.09	0.09	0.27
0.32	0.528	3.277	40.0	17.0	0.85	-0.15	0.15	0.45
0.50	0.825	3.084	35.0	18.0	0.69	-0.31	0.27	0.49
1.00	1.650	2.790	33.0	20.0	0.64	-0.36	0.33	1.05
1.50	2.475	2.605	27.0	23.0	0.47	-0.53	0.38	1.44
2.00	3.300	2.381	24.5	26.0	0.41	-0.59	0.45	1.63
2.50	4.125	2.385	21.0	28.0	0.36	-0.64	0.48	1.76
3.00	4.950	2.304	16.0	35.0	0.25	-0.75	0.69	2.10
3.50	5.775	2.233	14.0	36.0	0.21	-0.79	0.73	2.31
4.00	6.600	2.180	12.0	39.0	0.17	-0.83	0.81	2.47
4.50	7.425	2.129	8.0	42.0	0.11	-0.89	0.88	2.66
5.00	8.250	2.083	4.0	43.0	0.05	-0.95	0.94	2.80

*The SO₄²⁻ concentration was calculated from the dissociation constant of sulphuric acid, 4.96 × 10⁻³, which was obtained from the thermodynamic constant of 1.2 × 10⁻² allowing for the activity coefficients at I = 3; the latter was calculated from the Lewis approximate formula⁶.

The result obtained shows that in the range of greatest absorption tellurium forms the complex Te(SO₄)₃²⁻.

In determining the stability constants of the tellurium sulphato-complexes we used a method⁴ which allows ion-exchange chromatographic results to be used to find the relation between the formation function \bar{n} (the mean number of ligands connected with the central ion)⁵ and the concentration of the free ions of the ligand under the condition that the complexes formed are not absorbed by the cation-exchange resin.

In calculating \bar{n} , the formula:

$$\bar{n} = \frac{q_+(\gamma_+ - 1) + q_- \gamma_-}{Z_A}$$

was used, in which q_+ is the charge of the central ion (+4); q_- the charge of the anionic complex formed under the conditions of greatest absorption of the test element by the anion-exchange resin (-2); Z_A is the magnitude of the charge of the ligand; ($Z_A = 2$); γ_+ the relative fraction of cationic species; and γ_- the relative fraction of anionic species⁵. The results of the calculations are given in the Table.

⁵ The quantities γ_+ and γ_- were calculated from the results in the Table, as shown earlier⁴.

The Table was used to construct a graph of $\bar{n} = f(\text{SO}_4^{2-})$ and then find the following quantities, needed for calculating the stability constants of the complexes by the Bjerrum method⁵:

$$\beta = \left(\frac{1}{[\text{SO}_4^{2-}]^{\bar{n}}} \right)_{\bar{n} = \frac{N}{z}} = 3.55 \times 10^2 \quad (N = 3),$$

$$\frac{d\bar{n}}{d\log[\text{SO}_4^{2-}]} = 2.20, \quad \Delta = 0.4343 \times 2.20 = 0.96,$$

$$\beta_n = \frac{N - n + 1}{n} \times 3.55 \times 10^2 \times 0.78^{N+1-2n}.$$

Calculation gave the following constants:

$$\beta_1 = \frac{[\text{Te}(\text{SO}_4)_2^{2+}]}{[\text{Te}^{4+}][\text{SO}_4^{2-}]} = 6.5 \times 10^2,$$

$$\beta_2 = \frac{[\text{Te}(\text{SO}_4)_3^0]}{[\text{Te}(\text{SO}_4)_2^{2+}][\text{SO}_4^{2-}]} = 3.6 \times 10^2,$$

$$\beta_3 = \frac{[\text{Te}(\text{SO}_4)_3^{2-}]}{[\text{Te}(\text{SO}_4)_2^0][\text{SO}_4^{2-}]} = 2.0 \times 10^2.$$

REFERENCES

1. A.A.Kudryavtsev, "Khimiya i Tekhnologiya Selena i Tellura" (Chemistry and Technology of Selenium and Tellurium), Izd. Metallurgiya, Moscow, 1968.
2. B.I.Nabivanets, E.E.Kapantsyan, and E.N.Oganesyan, Zhur. Neorg. Khim., 19, 729 (1974) [Russ. J. Inorg. Chem., No. 3 (1974)].
3. I.E.Blyum, A.F.Glazkova, and G.A.Sysoeva, "Metodicheskie Materialy dlya Laboratorii Geologicheskikh Upravlenii i Ekspeditsii" (Methodological Materials for Laboratories of Geological Operations and Expeditions), Bulletin No. 8, 184 (1968).
4. B.I.Nabivanets, Ukrain. Khim. Zhur., 32, 886 (1966).
5. J.Bjerrum, "Metal Ammine Formation in Aqueous Solution" (Translated into Russian), Inostr. Lit., Moscow, 1961.
6. Yu.Yu.Lur'e, "Spravochnik po Analiticheskoi Khimii" (Handbook on Analytical Chemistry), Izd. Khimiya, Moscow, 1971, p. 107.