

The Existence of Selenium Dithizonate

By J. STARÝ* and J. MAREK

(Department of Nuclear Chemistry, Technical University of Prague, Praha 1, Břehová 7, Czechoslovakia)

Summary The extraction of selenium(IV) (labelled with ^{76}Se) by dithizone (H_2Dz) solutions in carbon tetrachloride has been systematically studied, and from the results obtained the composition of the extractable species, $\text{Se}(\text{HDz})_4$, has been inferred.

RECENTLY, a paper¹ "The Non-existence of Selenium Dithizonate" was published in this journal. The authors concluded on the basis of spectrophotometric measurements that selenium dithizonate does not exist and consequently was not extracted into carbon tetrachloride.

In our department, a systematic study of the extraction by dithizone solution of selenium(IV) labelled with ^{76}Se was carried out two years ago.² This investigation has been extended by some additional results.

First of all, the kinetics of the extraction of traces of selenium by pure carbon tetrachloride as well as by dithizone solutions in the same solvent has been investigated in detail. It was found that time needed for reaching the extraction equilibrium strongly increases with the decrease of dithizone concentration in carbon tetrachloride $[\text{H}_2\text{Dz}]_{\text{org}}$

and with the decrease of hydrochloric acid concentration.

Further, the influence of selenium concentration has been investigated. It was found that the distribution ratio q did not depend on the selenium concentration (10^{-10} — 5×10^{-5} M); thus no polynuclear complexes were formed in the aqueous as well as in the organic phases.

The composition of the extracted species is inferred from the dependence $\log q = f(\log [\text{H}_2\text{Dz}]_{\text{org}})$. In 1M-hydrochloric acid, the slope of the curve equals 3.96 for $[\text{H}_2\text{Dz}]_{\text{org}} > 5 \times 10^{-5}$ M; thus a complex $\text{Se}(\text{HDz})_4$ is extracted into the organic phase.

To verify the composition of selenium dithizonate, 0.5 μmole of selenium(IV) labelled with ^{76}Se in 5M-hydrochloric acid was successively extracted by three 0.5 μmole portions of dithizone for 3 min. From the activities of organic extracts isolated it was found that the ratio $\text{Se}:\text{H}_2\text{Dz}$ in the complex equals 1:4.2, 1:4.1, and 1:4.1 respectively.

From the results given in the present as well as in the previous paper³ it is evident that selenium is extracted by dithizone solutions in carbon tetrachloride as a complex $\text{Se}(\text{HDz})_4$.

(Received, January 12th, 1970; Com. 038.)

¹ R. S. Ramakrishna and H. M. N. H. Irving, *Chem. Comm.*, 1969, 1356.

² J. Marek, Thesis, Technical University of Prague, 1968.

³ J. Starý and J. Růžička, *Talanta*, 1968, 15, 505.