Adsorption of Thorium and its TTA-complexes from Aqueous Solutions

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The adsorption of trace concentrations of thorium on glass is found to be independent of acidity up to pH 1, but increases thereafter to a maximum at pH 4.2. The Th-thenoyltrifluoroacetone complex is similarly adsorbed, but two maxima are observed, at pH 3.2 and 7.0. Adsorption on other materials such as stainless steel, gold, platinum, polypropylene, polyethylene, and teflon was also studied. Particularly high adsorption was found for the Th-complex on teflon.

In a study of complex formation between trace amounts of Th(IV) and theonyltrifluoroacetone (HTTA) in various solvent systems,[1] adsorption was found to interfere seriously with the investigation. A separate study was therefore undertaken in order to control the adsorption conditions. Similar investigations in other systems have been reported by Rydberg[2] and by Adler and Stiegman[3] on Th(IV), and by King[4] and Haissinsky[5] on Pu(IV), which exhibits similar behavior to Th(IV).

The adsorption depends on the surface properties and the conditions in the solution. It is usually found that the adsorption increases with decreasing concentration of the metal and with increasing pH up to a maximum at pH 4—6. Even though the results can often be qualitatively explained, it is at present not possible to predict the adsorption quantitatively, one reason being that the adsorption probably occurs by a number of different mechanisms, as indicated below.

EXPERIMENTAL

Chemicals. $^{234}Th(UX_1)$ was isolated from uranyl nitrate by a cation exchange method described by Murase.[6] The purity of thorium was controlled by measuring its half-life and gamma spectrum. Because no carrier thorium was added, the thorium concentration was never above 2.4×10^{-10} M. All other chemicals were of *p.a.* quality. The glass plates (area 2 cm²) and the pipettes (volume 2 ml) were made of sodium glass. They were cleaned with acid dichromate solution and washed with alcohol and water before use. The stainless

steel and platinum plates were polished and washed with HNO_3. The bright gold plates were cleaned with alcohol as were all plastic plates. All material was dried before use.

Radioactive measurements. [234]Th-detection was made on the gamma radiation and the bremsstrahlung from [234]Pa(UX_2) using a Picker Nuclear well-type scintillation counter. By waiting 20 min before measurement it was ensured that equilibrium was always established between [234]Th and its daughter [234]Pa. The pH was measured with a combined glass electrode, Radiometer GK 2021 C, and a Radiometer type 26 potentiometer.

In general, approximate scatter of $\pm 10\%$ was found in the adsorption measurements, even when the statistical error in the activity measurements was much smaller.

Adsorption on plates. Adsorption on the plates was investigated by keeping the plates for some time in solutions of specific composition. After removal from the solutions, they were washed with distilled water. The reverse side of the plates were always covered with tape, which was removed after the washing. The plates were allowed to dry before measurement was carried out.

The extent of adsorption was studied for the following conditions: (1) glass, 0.1 — 3.0 M $HClO_4$, 3 h; (2) glass, 0.1 M $NaClO_4$, pH 1—7, 3 h; and (3) different materials, 0.1 M $NaClO_4$, pH 5.0, 0.001 M TTA, 4 h. Adsorption takes place so rapidly that the different times used are unimportant. The value pH 5 was chosen because complex formation between Th(IV) and TTA is at a maximum here, *i.e.* practically all Th(IV) is in the form of Th(TTA)$_4$ complex.[1]

Adsorption on pipettes. To measure the adsorption of Th in pipetting, the solution containing a trace concentration of thorium was sucked up into a 2 ml pipette and kept there for 1 min, after which the solution was allowed to run out into a measuring vessel. The pipette was washed with 2 ml distilled water. These combined solutions gave the radioactive R_s cpm. The adsorbed thorium in the pipette was measured after crushing the pipette and including the broken glass into another measuring vessel, giving R_a cpm. The percentage adsorbed is equal to $100(R_a/R_s + R_a)$. The extent of adsorption was studied for the following conditions: (1) 0.1 M $NaClO_4$, pH 4.2, temperature 15—60°C, and (2) 0.001 M TTA, 0.1 M $NaClO_4$, pH 1—8. All experiments were done at 25°C unless otherwise specified.

RESULTS

Adsorption on glass. Ordinary glass may be regarded as containing weakly acidic SiOH groups, in which the hydrogen dissociates with increasing pH. The surface will then act as a cation exchanger for trace amounts of metals. It is therefore to be expected that Th^{4+} will be increasingly adsorbed on the glass with increasing pH. The experiments showed a constant adsorption for 3.0—0.1 M $HClO_4$, but it then increased with the pH up to about 4.2, see Fig. 1. The decrease at still higher pH can be explained if it is assumed that the Th-hydrolysis has proceeded so far by then that almost only uncharged
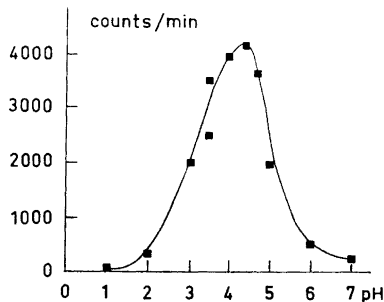

Fig. 1. The pH-dependence of thorium adsorption on sodium glass from a carrier-free tracer solution. Ionic strength 0.1 M $NaClO_4$.

or negatively charged Th-complexes, which have a smaller tendency for adsorption, are formed.

The effect of temperature at the adsorption maximum is shown in Fig. 2. The increased adsorption may be due to the fact that the weak acid groups of the glass become dissociated and that Th-hydrolysis is suppressed at higher temperatures.
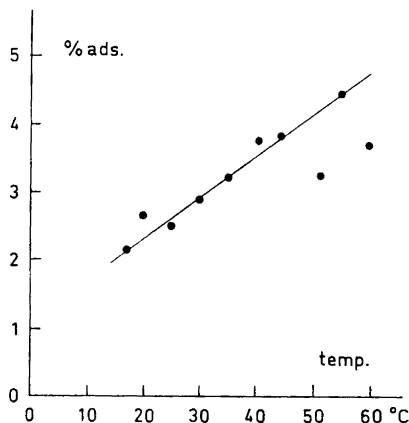

Fig. 2. Percentage thorium adsorbed on a pipette as a function of temperature at pH 4.5 and ionic strength 0.1 M NaClO$_4$.
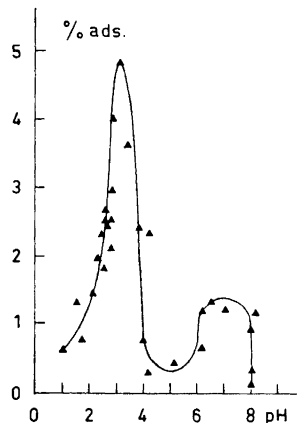
Fig. 3. Percentage thorium adsorbed on a pipette as a function of pH. [HTTA]=0.9 mM and ionic strength 0.1 M NaClO$_4$.

Fig. 3 shows the extent of adsorption in the presence of the chelating agent HTTA as a function of pH. The first maximum at pH 3.2 may be explained as above. Because the maximum occurs earlier than in Fig. 1, and it is known that the TTA-complexes dominate over the OH-complexes, it must be assumed that the Th-TTA-complexes are more strongly adsorbed than the corresponding OH-complexes. The second maximum is unexpected and has not been reported by other authors. One explanation may be that the glass contains a second weak acid group with strong adsorption properties. Another explanation is that the glass has a basic group, which acts as an anion exchanger for negatively charged hydroxy complexes, which begin to compete with the Th(TTA)$_4$-complexes at pH 6. Neither of these explanations is very satisfactory.

Adsorption on other materials. The results from the adsorption studies on different materials are presented in Table 1. The high adsorption of the Th-TTA-complex on teflon may be due to the fact that the TTA molecule is rather similar to the teflon molecule: teflon consists of $-(CF_2-CF_2)_n-$ and TTA of $C-C-CF_3$ groups. The adsorption is also high for polypropylene and polyethylene which may be due to the fact that these plastic materials contain plastizisers, which may extract the thorium complex into the plastic material.

Table 1. Adsorption of ^{234}Th as TTA complex on different materials in 0.1 M NaClO$_4$ at pH 5.

Material	Relative values
Stainless steel	0.7
Glass	1.0
Gold	2.2
Platinum	6.6
Polypropylene	7.2
Polyethylene	9.9
Teflon	10.6

Desorption of thorium. It is often important to remove the radioactivity adsorbed on laboratory equipment. To find a suitable decontamination solution for the Th(IV)-experiments, a number of glass plates (Pyrex) with adsorbed thorium (UX$_1$) were washed with different cleaning liquids for 5 min. The activity on the glass plates was measured before and after the washing. The results are given in Table 2.

Table 2. Effect of different washing liquids on glass plates containing adsorbed ^{234}Th.

Washing liquid	Percentage activity removed by washing for 5 min
0.1 M HClO$_4$	88
Dichromic sulfuric acid	99
RBS (dishwashing detergent)	53
Flink » »	29
0.1 M TTA in EtOH	42
0.1 M Th(NO$_3$)$_4$ in 0.1 M HClO$_4$	52
EtOH + 0.1 M HClO$_4$	25

The results show that basic solutions such as RBS and Flink are less effective than the acids. The result is probably due to the fact that the hydrogen ions in the acid solutions replace the positive ions adsorbed on the glass surfaces.

To prevent adsorption from a solution it is necessary to use a carrier. For this purpose thorium, hafnium, and zirconium nitrates were found to be excellent, in agreement with the results found by Adler and Stiegman.[3] Here the positive carrier ions compete with UX$_1$ in the adsorption process. When the carrier ions are in great excess compared with UX$_1$ this method is very effective.

REFERENCES

1. Edroth, B. *To be published.*
2. Rydberg, J. *Svensk Kem. Tidskr.* **64** (1952) 199.
3. Adler, I. and Stiegman, J. *J. Am. Chem. Soc.* **57** (1953) 443.
4. King, E. *U.S.A.E.C. Report MDDC-393* (1946).
5. Haissinksy, M. *J. Chim. Phys.* **55** (1958) 510.
6. Murase, T., Lind, E. and Nelson, F. *J. Chromatog.* **14** (1964) 478.

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