On the Chemically Induced Decay Constant Variation of Tc-99 m

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The chemical induced decay constant variations for some complex compounds of Tc-99 m were measured by means of a semidifferential approach, using the scintillation technique. The results are

$$
\begin{aligned}
\lambda(\mathrm{TcO_4^-}) - \lambda(\mathrm{TcCl_6^{2-}}) &= (2.52 \pm 0.30) \cdot 10^{-3}\,\lambda\,,\\
\lambda(\mathrm{TcCl_6^{2-}}) - \lambda(\mathrm{TcBr_6^{2-}}) &= (-0.02 \pm 0.20) \cdot 10^{-3}\,\lambda\,,\\
\lambda(\mathrm{TcCl_6^{2-}}) - \lambda(\mathrm{TcI_6^{2-}}) &= (0.78 \pm 0.41) \cdot 10^{-3}\,\lambda\,,\\
\lambda(\mathrm{TcO_4^-}) - \lambda(\mathrm{TcI_6^{2-}}) &= (3.30 \pm 0.30) \cdot 10^{-3}\,\lambda\,,\\
\lambda(\mathrm{TcO_4^-}) - \lambda(\mathrm{TcBr_6^{2-}}) &= (2.50 \pm 0.41) \cdot 10^{-3}\,\lambda\,.
\end{aligned}
$$

Theoretical estimations by means of atomic structure calculations show that $\mathrm{TcO_4^-}$ should have the greatest decay constant among the compounds investigated, in accordance with the measured values, and that the decay constants of the octahedral complexes should follow the spectrochemical series, partly confirmed by the experiments.

1. Introduction

The nuclear isomeric state Tc-99m exhibits advantageous conditions for studying the influence of the chemical environment on nuclear decay due to its conveniently measurable half life, high internal conversion coefficient (ICC) and position in the periodic table. In previous work evidence was given on effects of the chemical environment as well as of pressure, temperature and electric fields on the decay constant [1–6]. The measured values are between some 10^{-5} (electric fields) and some 10^{-3} (chemical environment). A simple relation between the decay constant and the electron density close to the nucleus (as with electron capture) does not exist for the E3-transition of Tc-99m so that quantitative conclusions concerning structure could not be drawn from the measured values [1–6]. As for effects of pressure, however, theoretical values were given [7] which correspond to the experimental ones [2].

Bainbridge [1] found the decay constant of the heptavalent pertechnetate to be higher by 3 per mille than that of metallic technetium. It is to be expected, however, that the higher-valent compound has the smaller decay constant because of the smaller electron density near the nucleus. Bainbridge's result was attributed by Slater [8] to the smaller Tc-Tc-distance in $\mathrm{TcO_4^-}$ in comparison to that in the metal and by Perlman [9] to a readjustment of the core overcompensating the delocalization in the valence shell.

In the present work the influence of the chemical environment on the decay constant of Tc-99 is investigated in order to find out possible consequences of the effects concerning structure analysis.

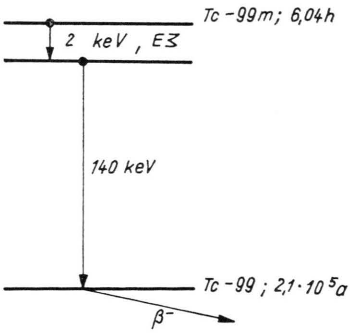

Fig. 1. $^{99\mathrm{m}}$Tc decay scheme.

2. Experimental

2.1. Principle of Measurement

The measurements were performed using a "semidifferential approach" [10] proposed by Huber et al. [11]. According to this method, the two samples representing different chemical compounds of the nucleus in question are measured alternately by the same measuring channel, and the decay constant variation $\Delta\lambda/\lambda$ can be determined from a plot of the activity ratio against time. The 140 keV secondary radiation of the 2 keV transition in question was measured by the conventional

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scintillation technique with a low discriminating threshold (1.5 × 1.5 inch NaI(Tl) crystals, RCA 8575-type multiplier). With a total measuring time of $2/\lambda$ and an initial rate of 8×10^4 counts per second the mean square error $\delta(\Delta\lambda/\lambda)$ amounts to 5×10^{-5} [11, 12]. The time of a single measurement was chosen to be 9.8 min, sample change took 0.2 min. The counts were alternately averaged according to [11], using, however, the geometric mean, which suits the exponential function better than the arithmetic one.

2.2. Systematic Errors

2.2.1. Dead Time

The dependence of the counting rate on time is

$$F(t) = \frac{z_1(t)}{z_2(t)} = \frac{z_1(0)}{z_2(0)} \cdot \frac{e^{-(\lambda+\Delta\lambda)\cdot t}}{e^{-\lambda t}} \approx F(0)\{1 - \Delta\lambda\, t\} \tag{1}$$

and $\Delta\lambda/\lambda$ is found from the relation

$$\Delta\lambda/\lambda = (F(0) - F(t))\big/\lambda t \cdot F(0)\,. \tag{2}$$

If there is a distortion $\delta F = \tilde{F} - F$ of the (approximately) linear shape of the function $F(t)$ due to dead time and/or background, there follows

$$\delta\left(\frac{\Delta\lambda}{\lambda}\right) = \frac{1 - \Delta\lambda \cdot t}{\lambda t}\left\{\frac{\tilde{F}(0)}{F(0)} - \frac{\tilde{F}(t)}{F(t)}\right\}. \tag{3}$$

In general, the initial counts of the two samples differ by a factor $(1+\eta)$:

$$z_2(0) = z_1(0)\cdot(1+\eta) = z(0)\cdot(1+\eta)\,. \tag{4}$$

Omitting a dead time correction, with $\Delta\lambda = 0$ we have the erroneous ratios

$$\begin{aligned} \tilde{F}(0) &= \frac{z(0)}{1 + z(0)\,\tau}\Big/\frac{z(0)(1+\eta)}{1 + z(0)(1+\eta)\,\tau} \approx F(0)\cdot(1 + \eta\, z(0)\,\tau)\,, \\ \tilde{F}\left(\frac{2}{\lambda}\right) &= \frac{e^{-2}\,z(0)}{1 + e^{-2}\,z(0)\,\tau}\Big/\frac{e^{-2}\,z(0)(1+\eta)}{1 + e^{-2}\,z(0)(1+\eta)\,\tau} \approx F\left(\frac{2}{\lambda}\right)\cdot(1 + \eta\, e^{-2}\,z(0)\,\tau)\,, \end{aligned} \tag{5}$$

and with (3) at $t = 2/\lambda$

$$\delta_\tau\left(\frac{\Delta\lambda}{\lambda}\right) \approx \frac{1 - e^{-2}}{2}\,\tau\,\eta\, z(0)\,. \tag{6}$$

As a numerical example, with $z(0) = 8 \times 10^4\ \mathrm{s}^{-1}$, $\eta = 10^{-2}$ and $\tau = 1.5\ \mu\mathrm{s}$ we have $\delta_\tau(\Delta\lambda/\lambda) = 5.2 \times 10^{-4}$. The dead time losses were determined according to Martin [13] with an exactness of one percent [14] and corrected, and the two samples were balanced (by distance variation) up to $\eta = 10^{-3}$ so that $\delta_\tau(\Delta\lambda/\lambda) = 5.2 \times 10^{-7}$, which could be neglected.

2.2.2. Background

Omitting a correction of the background U, which is constant in time, with $\Delta\lambda = 0$ we have the erroneous ratios

$$\begin{aligned} \tilde{F}(0) &= \frac{z(0) + U_1}{(1+\eta)\,z(0) + U_2}\,, \\ \tilde{F}\left(\frac{2}{\lambda}\right) &= \frac{z(0)\,e^{-2} + U_1}{(1+\eta)\,e^{-2}\,z(0) + U_2}\,, \end{aligned} \tag{7}$$

and, as above, there follows

$$\delta_{\mathrm{u}}\left(\frac{\Delta\lambda}{\lambda}\right) = \frac{e^2 - 1}{2}\left\{\frac{U_2}{z_2(0)} - \frac{U_1}{z_1(0)}\right\}. \tag{8}$$

For the room background, $U_2 = U_1 = U$, therefore

$$\delta_{\mathrm{u}}\left(\frac{\Delta\lambda}{\lambda}\right) = \frac{e^2 - 1}{2}\cdot\frac{U}{z(0)}\,\eta\,, \tag{9}$$

and with $U/z(0) = 1.25 \times 10^{-3}$ and $\eta = 10^{-3}$ an incorrectly corrected room background will not be critical. In the same way equal concentrations of radioactive impurities in both samples are of no consequence. If, on the other hand, there are differences in the radioactive impurities of the samples, according to Eq. (8) a $\Delta\lambda/\lambda$ value is simulated. By means of γ-ray spectrometric analysis impurities of Mo-99, Ce-141, Te-132, I-131, Ru-103 and Nb-95 in total concentrations from 1.3×10^{-5} to 10^{-4} relative to the Tc-99m content and to the elution time were found in our samples. Because the measurements were often started about 20 hours after elution (see 2.2.3) and because of the low energy discrimination threshold (see 2.1) the effective impurity contributions were much higher. They could be measured only after the decay of the Tc-99m and therefore had to be corrected for their own decay. The reduced values lay in the interval from 5×10^{-5} to 8×10^{-4}. Thus we found that even the two samples obtained from the same eluate exhibit different amounts of radioactive impurities. The differences lay in the interval $(1 \ldots 20) \times 10^{-5}$, which indicates the importance of the impurity correction according to Equation (8).

2.2.3. Geometric Effects

When the semidifferential measurements were started immediately after sample preparation, there was often no reproducibility in the $F(t)$ plot at $t \leqq 10$ h. An analysis of experimental decay curves corrected with respect to dead time, background and impurities showed deviations up to a few per cent in both directions from the theoretical exponential curve, in general different for the two samples (Figure 2). These effects are found only with liquid samples. Hence, they cannot be interpreted as being due to electronic shifts but only to displacements of the individual radiation sources in the samples. (Diameter of vessels 20 mm, distance between detector and vessel centres 20 mm.)

15 hours after sample preparation, the $F(t)$ plots show a linear and reproducible characteristic.

2.2.4. "Null" Experiments

For revealing systematic errors 14 control measurements with 2 solid Co-57 standard preparations of the same kind and 7 control measurements with pairs of chemically identical Tc-99m samples were performed. The systematic error calculated from these 21 measurements amounted to $\Delta\lambda/\lambda = (-3 \pm 3) \times 10^{-5}$ with a 95% confidence level.

2.3. *Sample Preparation*

The Tc-99m initial substance was extracted from technetium generators (producer: ZfK Rossendorf) by milking with 0.1 n-HCl and mixed with 10^{-4} mol/l $NH_4{}^{99}TcO_4$ solution carrier. The concentrations of radionuclide impurities in the eluate, measured by γ-ray spectrometry, varied in the interval $3 \times 10^{-4} \ldots 10^{-3}$, thus before the sample preparation a purification was necessary. To this end a separation procedure for technetium from fission products based on the solvent extraction technique by N. Trautmann et al. [15] was modified. The purities achieved are given in Sect. 2.2.2. (At present the purification procedure is being improved [16].) After passing a chromatographic column the $TcO_4{}^-$ eluate is dissolved in $2n$ HNO_3. This solution is either used as $TcO_4{}^-$ measuring samples (3 ml and 75 µCi activity) or is changed into hexahalogenotechnetium complexes.

For the preparation of $TcCl_6{}^{2-}$ the $TcO_4{}^-$ is reduced by means of $SnCl_2$ solution in concentrated HCl (1 g $SnCl_2$ in 10 ml conc. HCl) in excess, with the colour changing into yellow. For the preparation of $TcBr_6{}^{2-}$ and $TcI_6{}^{2-}$ concentrated HBr or HI is used as reducing agent, the colourless solutions turning into orange and brown, respectively.

3. Results

For checking purposes the apparatus was equipped with a second independent measuring line. Thus each run could be carried out as a double

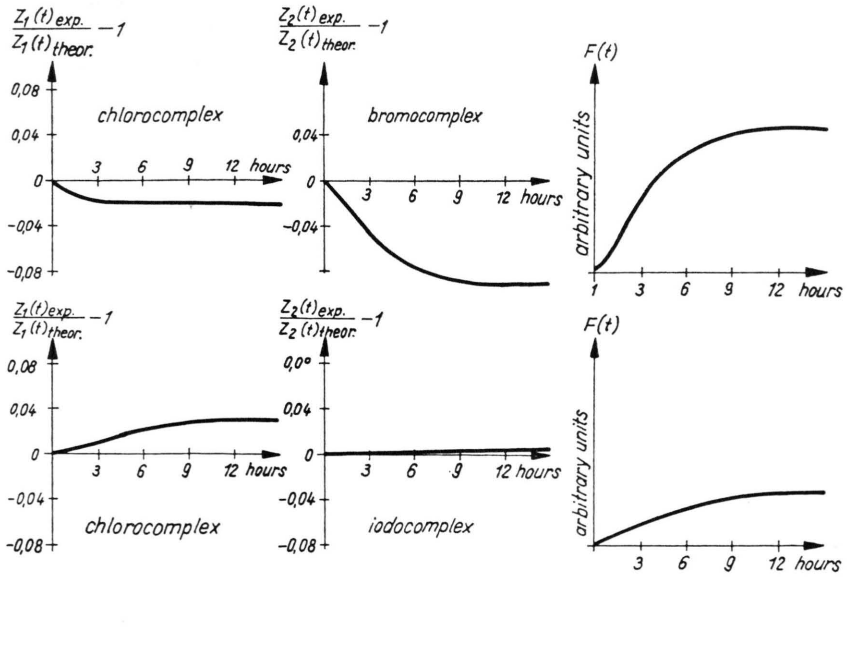

Fig. 2. Nonlinearities in normalized decay curves and in $F(t)$.

Table 1. Experimental and corrected values of decay constant variation.

Problem	n_i	$\left(\frac{\Delta\lambda}{\lambda} \pm t \cdot \frac{\sigma}{\sqrt{n}}\right) / {}^0/_{00}$	$\left(\frac{\Delta\lambda}{\lambda} \pm t \cdot \frac{s}{\sqrt{n}}\right) / {}^0/_{00}$	cf. text
$[TcO_4]^-$ — $[TcCl_6]^{--}$	7	2.48 ± 0.26	2.52 ± 0,30	2.4
$[TcCl_6]^{--}$ — $[TcBr_6]^{--}$	13	− 0.11 ± 0.23	− 0.02 ± 0.20	0.0
$[TcCl_6]^{--}$ — $[TcI_6]^{--}$	5	0.92 ± 0.51	0.78 ± 0.41	0.8
$[TcO_4]^-$ — $[TcI_6]^{--}$	7	3.16 ± 0.33	3.30 ± 0.30	3.3
$[TcO_4]^-$ — $[TcBr_6]^{--}$	5	2.66 ± 0.60	2.50 ± 0.41	

measurement. Measurements which showed no linearity in the $F(t)$ plot despite dead-time, background and impurity correction revealed geometric effects or insufficient corrections and were rejected. Moreover, a 3σ test was applied. The results are listed in the table 1.

In column 2 the number of single measurements is given.

The average of $\Delta\lambda/\lambda$ (error with Student's factor with a 95% confidence level) is given in column 3. The values of column 3 were corrected for the systematic error (cf. 2.2.4) and subjected to a balancing calculation, since they are related by the expressions

$$g \equiv (\Delta\lambda/\lambda)_{O_4-Cl_6} + (\Delta\lambda/\lambda)_{Cl_6-Br_6} - (\Delta\lambda/\lambda)_{O_4-Br_6} = 0 \qquad (9\text{a})$$

and

$$h \equiv (\Delta\lambda/\lambda)_{O_4-I_6} - (\Delta\lambda/\lambda)_{Cl_6-I_6} - (\Delta\lambda/\lambda)_{O_4-Cl_6} = 0 \,. \qquad (9\text{b})$$

The balancing calculation consists in minimisation of the expression

$$\sum_i \sum_j (x_{ij} - x_i)^2 - \mu\, g - \nu\, h \,, \qquad (10)$$

where the subscript j runs over all measurements of a problem from 1 to n_j; μ and ν are Lagrange parameters and x_i are the desired final results $\Delta\lambda/\lambda$. The latter are given in column 4 together with their errors with a 95% confidence level. s denotes the mean error of the measuring method, resulting from the differences between the 37 single measurements and their balanced group averages x_i according to

$$s = \sqrt{\frac{\sum\limits_{i=1}^{6} \sum\limits_{j=1}^{n_j} (x_{ij} - x_i)^2}{\sum n_i - 6}} \,. \qquad (11)$$

(In computing this quantity control measurements of chemically identical samples were considered, too.)

Furthermore, for each sample the decay constant λ was evaluated from the corrected decay curves. From the mean values relative differences were calculated; they are given in column 5 and agree with the values in column 4, which should be expected in the absence of electronic drifts.

4. Theoretical Estimation

According to the well-known relations

$$\lambda = \lambda_\gamma (1 + \alpha) \,, \qquad (12)$$

$$\frac{\Delta\lambda}{\lambda} = \frac{1}{1+\alpha} \Delta\alpha \approx \frac{\Delta\alpha}{\alpha} \quad (\text{with } \alpha \gg 1) \qquad (13)$$

the decay rate variation of highly converted transitions is given as the relative variation of the internal conversion coefficient ICC. An estimation of the order of magnitude of chemically induced decay rate variations is obtained by the investigation of the dependence of the ICC on the ionicity of the free atom. At first the partial ICC's for the Tc-99m 2.17 keV transition were calculated by means of the computer program described in [17]. The values are given in Table 2. The partial ICC are listed in column 2, and the relative partial ICC's are listed in column 3.

For energetic reasons the K and L shell are excluded from conversion, and because of the

Table 2. Partial ICC's of Tc-99 m ($4\,d^{*4}\,4\,d^1\,5\,s^2$).

i	α_{i0}	α_{i0}/α
$3\,p^{*2}$	3.28×10^9	0.236
$3\,p^4$	5.82×10^9	0.419
$3\,d^{*4}$	1.25×10^9	0.090
$3\,d^6$	1.88×10^9	0.135
$4\,p^{*2}$	5.48×10^8	0.039
$4\,p^4$	9.57×10^8	0.069
$4\,d^{*4}$	1.36×10^8	0.010
$4\,d^1$	3.09×10^7	0.002
	1.39×10^{10}	1.000

E3 character of the transition the conversion in s shells can be neglected. Therefore, in contrast to EC and IC M1 processes in the case of Tc-99m there is no immediate connection between decay constant and s-electron density at the site of the nucleus, and if the latter changes, no influence on the decay constant is to be expected, apart from small core reorganization effects. However, though the 4d electrons do not contribute to the electron density at the nucleus, their density changes must influence the decay constant. According to Table 2, in the frozen core approximation a decrease of the decay constant by 1.2% should be expected if all five 4d electrons are removed.

However, owing to the high contribution of the M and N shells to the total ICC, core reorganization effects have to be considered. This can be done approximately by the relation [18]

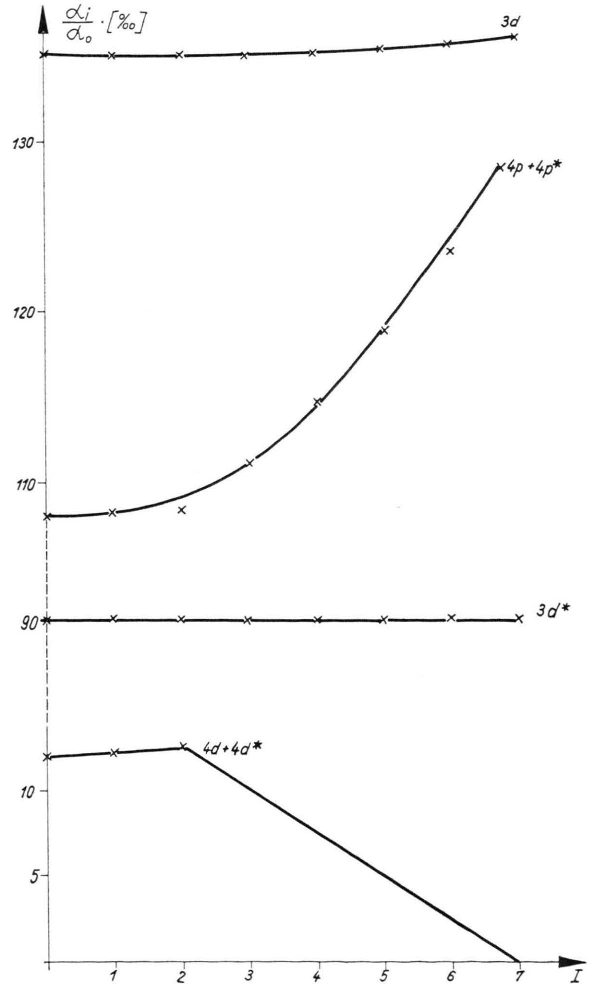

Fig. 3. Relative partial ICC's as function of ionicity.

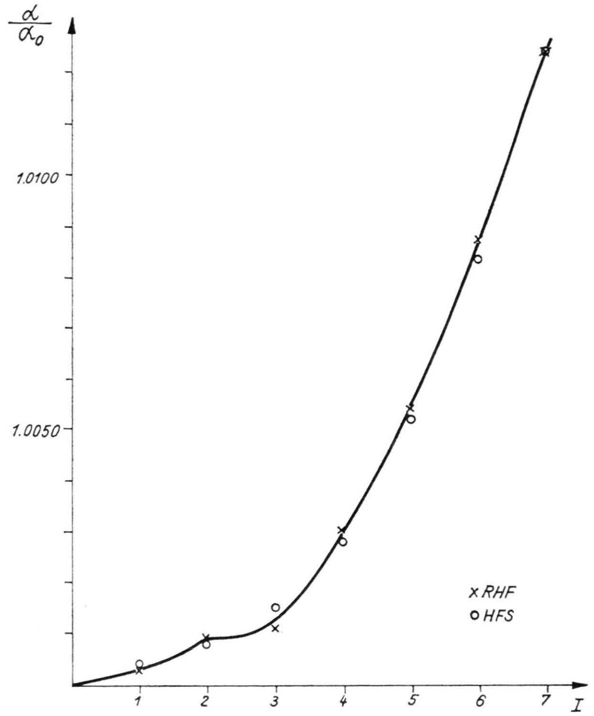

Fig. 4. Relative total ICC as function of ionicity.

$$\alpha_i = \frac{\alpha_{i0}}{|\psi_{i0}(R)|^2} \cdot |\psi_i(R)|^2 , \qquad (14)$$

where α_i is the partial ICC, $|\psi_i(R)|^2$ the electron density at the nuclear surface of the subshell in question*, and the subscript 0 indicates the ground state of the electron cloud. Equation (14) was evaluated by means of the DF programme by Desclaux [19] for all relevant subshells of Tc for the ionicities $I = 7 - n_{5s} - n_{4d} = 0 \ldots 7$, setting α_{4d} proportional to the occupation number n_{4d} according to Table 2. The results for the outer shells are given in Figure 3, in which the curves for $\alpha_{4p1/2}$ and $\alpha_{4p3/2}$ could be taken together to an α_{4p} curve due to their equivalent courses. As an interesting result we have an overcompensation of the α_{4d} effect by the α_{4p}, which is a typical screening effect.

The influence of ionicity on the total ICC is obtained by summing up all relevant subshells and is given in Figure 4.

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* Exact calculations of the ICC's by means of the local potential corresponding to the individual configuration are in progress.

At $I = 7$ we have $\Delta\alpha/\alpha = +1.24\%$, in contrast to the frozen core value -1.20%. This result speaks in favour of Perlman's [9] interpretation of Bainbridge's [1] TcO_4^- and technetium metal results.

The results represented in Fig. 4 by small circles were obtained with a spin-restricted evaluation of Eq. (14) by means of Herman and Skillman's HFS programme [20]. The reason for the good accordance of the relativistic and nonrelativistic shapes of function $\alpha(I)$ consists, on the one hand, in an equivalent dependence of the partial ICC's of both electron spin orientations on the ionicity according to spin-unrestricted Desclaux computations and, on the other hand, in the approximate compensating of relativistic effects in the electron density ratios of Equation (14). This fact allows us to consider more exactly the influence of the actual molecular environment by the use of MO programmes, though they are generally nonrelativistic: By means of the X_α-MT-SCF-SW approach [21] theoretical values for the decay rate variations of the measured technetium complexes are obtained [22].

5. Discussion

The results given in Table 2 are summarized in Figure 5. According to the relation following from Fig. 4, $\lambda(d^0) > \lambda(d^3)$, the greatest value of the investigated decay constants is to be expected for pertechnetate (d^0), which is in agreement with Bainbridge's [1] and our own experimental results. Because the $\alpha(I)$ plot is a curved line, we cannot exactly find the delocalisation ΔI from the experimental value $\Delta\lambda/\lambda = 2.52 \times 10^{-3}$ since we do not know the real position on the I scale of any of the measured ions. In the interval $3 \leq I \leq 6$ there holds $\Delta\lambda/\lambda = 2.8 \times 10^{-3}\,\Delta I$ to a good approximation, and in connection with the experimental value there would follow $\Delta I = 0.9$, in contrast to the formal ionic charge difference $\Delta I = 3$.

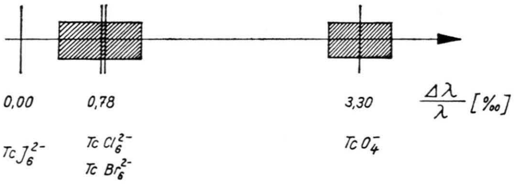

Fig. 5. Results for pertechnetate and halogenocomplexes (limits of experimental error hatched).

In the case of hexahalogenocomplexes, an influence of ligand species on the decay constant can also be expected: In the octahedral crystal field the t_{2g} electrons (configuration t_{2g}^3 for tetravalent complexes) are capable of forming π-bounds, the ligand π-acceptor ability, however, increasing according to the spectrochemical series [23]

$$I^- < Br^- < Cl^- < F^- .$$

Therefore the ionicity of the central ion and hence the decay constant should obey this series. Our measuring values confirm this in part. The measured equality between the chloro- and bromocomplex decay constants cannot be explained yet, and will be studied further.

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