

Ultraviolet spectrophotometry of rhenium compounds in water—speciation and concentration

Philip C. H. Mitchell

June 2009

Principles

For the purposes of REACH the rhenium species produced in water when rhenium compounds are dissolved or stirred in suspension may be identified by ultraviolet spectrometry of the water phase. Species are identified by their characteristic ultraviolet (uv) spectra. The position of an absorption peak and its intensity is characteristic of a species. The peak position is reported in wavenumbers (cm^{-1}) or nanometers (nm). The intensity is reported as a molar extinction coefficient, ϵ . For example the perrhenate ion $[\text{ReO}_4]^{2-}$ has an absorption maximum near $50\,000\text{ cm}^{-1}$ or 200 nm with a molar extinction coefficient $6500\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$. The measured light absorbance (A) of a solution is proportional to the concentration of the absorbing species, a relation expressed by Beer's law

$$A = \epsilon cl$$

where c is a concentration and l the linear thickness of the solution. For a given species the relation between absorbance and concentration is linear and so, knowing ϵ and l we can obtain the concentration of the species from the light absorbance of its solution. Alternatively by measuring the absorbance of a series of solutions of known concentrations of a species we can determine ϵ from a plot of absorbance against concentration. Experimentally the solution is placed in a glass or silica cell located in the spectrophotometer which records the light absorbed. Cells of various thicknesses (path lengths) are available (1, 5, 10 cm).

The uv spectrum of the $[\text{ReO}_4]^{2-}$ ion in sodium perrhenate solution has been reported, see Figure (A. Carrington, D. Schonland and M. C. R. Symons, J. Chem. Soc., 1957, 659).

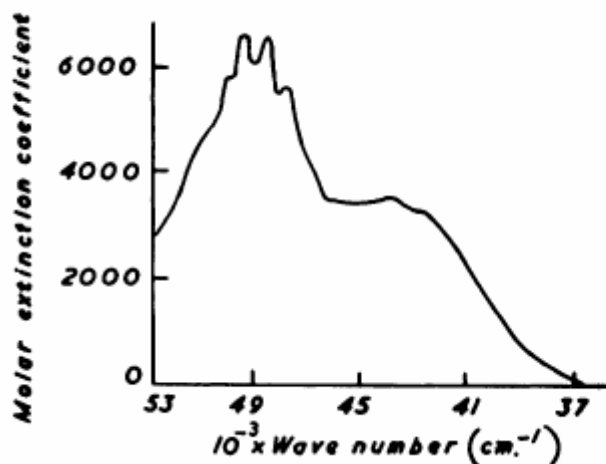


FIG. 4. Absorption spectrum of the aqueous perrhenate ion, ReO_4^- .

From Beer's law, taking $\epsilon = 6500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ from the Figure we calculate that an absorbance $A = 1$ will be provided by a concentration of $1.54 \times 10^{-4} \text{ mol } [\text{ReO}_4]^{2-} / \text{L}$ ($2.86 \times 10^{-2} \text{ g Re/L}$, 28.6 mg Re/L , 28.6 ppm) in a 1 cm cell. The absorbance of a 1 mg Re/L solution ($1.467 \text{ mg Na } [\text{ReO}_4]$) would be 0.035 in a 1 cm cell or 0.35 in a 10 cm cell.

Method

Measurement of uv spectra should be straightforward, routine, rapid and inexpensive in any well founded analytical laboratory. An OECD glp guideline has been published (OECD GUIDELINE FOR TESTING OF CHEMICALS 101"UV-VIS Absorption Spectra" (Spectrophotometric Method) 12 May 1981) and is attached. I recommend the following procedure.

1 Recording the perrhenate spectrum and the calibration of concentration vs absorbance

a Prepare an aqueous stock solution of 100 mg Re/L (as perrhenate) by dissolving 146.7 mg of NaReO_4 (0.5371 mmole) in ultrapure water making up to 1000 mL in a volumetric flask thermostatted at 20 °C.

b Prepare solutions of 1.0, 2.5, 5.0, 7.5 and 10.0 mg (Re)/L by diluting the stock solution as in the Table below. The expected light absorbances A for $\epsilon = 6500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ for various path length cells are shown in the Table, with the preferred cell selection in bold.

mg Re/L	1.000	2.500	5.000	7.500	10.000
mmol Re/L	0.005	0.013	0.027	0.040	0.054
mg NaReO_4/L	1.467	3.668	7.336	11.004	14.672
mL (100 mgRe/L) to be diluted to 1 L	10.000	25.000	50.000	75.000	100.000
absorbance 1 cm cell	0.035	0.087	0.175	0.262	0.349

absorbance 5 cm cell	0.175	0.436	0.873	1.309	1.745
absorbance 10 cm cell	0.349	0.873	1.745	2.618	3.491

c Record the spectrum of each solution in the range 180 to 500 nm.

d Locate the peak maximum (200-210 nm) and plot its absorbance vs concentration. The plot should be a straight line through the origin. This plot is the calibration for determining concentration from absorbance.

Note

Using analytically pure NaReO_4 we can assume that the rhenium concentrations are as made up but it might be desirable to check concentrations with a standard analytical method for Re, e.g. by the ICP-OES technique.

2 Recording the spectra of other rhenium compounds including insolubles

Rhenium substances for REACH are rhenium metal Re, perrhenic acid HReO_4 , ammonium perrhenate NH_4ReO_4 , rhenium heptoxide Re_2O_7 , sodium perrhenate NaReO_4 and rhenium heptasulfide Re_2S_7 . We wish to determine the solubilities (the concentration of rhenium in a saturated solution, i.e. a solution in equilibrium with undissolved solid) and the speciation (the rhenium species in the solution). From the uv spectrum of each solution we can determine the concentration of perrhenate and whether perrhenate is the only or dominant species (other species will give different spectra which can be interpreted). However we might consider the best procedure would be to determine solubilities (and reaction dissolution) by the standard glp method determining the total rhenium by, for example, ICP-OES and recording the uv spectrum of each solution (and pH). If we have just one species in solution (i.e. $[\text{ReO}_4]^{2-}$) then uv absorbance should correlate with the total rhenium.

For insolubles we might follow the procedure used for molybdenum compounds. Aqueous suspensions were prepared by adding ca 1 g of the compound to a volumetric flask of 500 mL. The suspensions were stirred at 20°C for 6, 12, 24, 48, 72 hours etc. Then a sample aliquot of 40 ml was taken out of the flask and filtered through a syringe filter with a porosity of 0.45 μm . The filtrates were used for pH and UV/vis measurements.

Note

In my view stirring with a magnetic follower is undesirable since it can cause attrition of the substance and possible colloid formation. The suspensions should be agitated in a thermostatic bath rather than stirred.

BEFORE THIS WORK IS CARRIED OUT I RECOMMEND DETAILED DISCUSSION WITH THE OPERATOR.

3 Recording uv spectra

a Use a double-beam spectrophotometer with a deuterium lamp as a light source.

b Use two matched cells of 1, 5 and 10 cm path length (see Table). The cells must be made of synthetic fused silica having excellent optical transmittance down to 180 nm. One cell is used for reference filled with ultrapure water; the other for the test solution.

c Cells can be cleaned with chromic acid (probably not necessary). Cells should be flushed several times with the blank and test solutions to ensure purity.

d Three spectra should be measured for each sample.

d Instrument parameters

Typical values are given in the Table below.

Working parameters of the UV/vis spectrophotometer

Parameter	Adjustment
Wavelength (start)	500 nm
Wavelength (stop)	200 nm
Average Time	0.1 s
Data interval	1 nm
Scan rate	600 nm/min
Source changeover	350 nm

PCHM 25 June 2009