Uv spectra of rhenium substances for REACH

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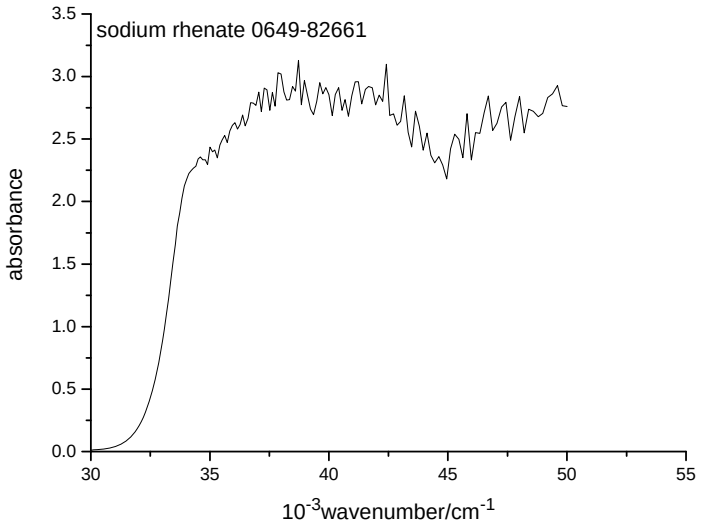
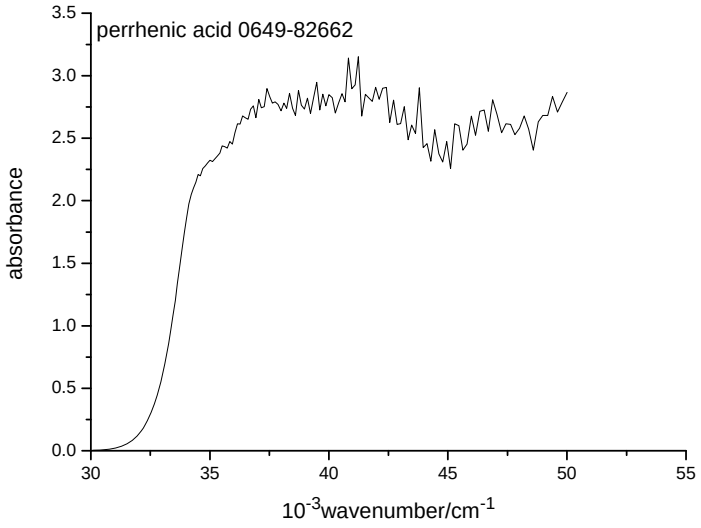
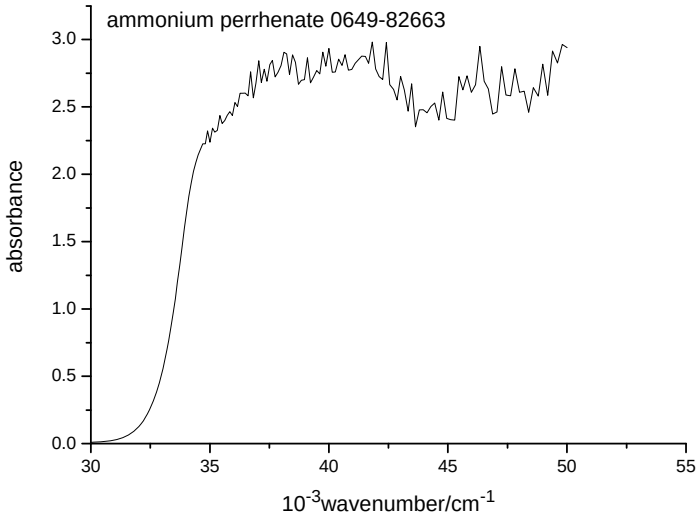
Preliminary Report

The uv spectra of rhenium substances for REACH are in Reports submitted by Aqura March 2010. I obtained the raw uv data as Excel files (wavelength, light absorbance) from Erin Logan and I have plotted and analysed the raw data using the Origin program. I show the spectra as wavenumber vs absorbance in the following figures, and calculate extinction coefficients, and comment. Absorption maxima are seen near 40000 and 50000 cm^{-1} with 'absorption' 3.0.







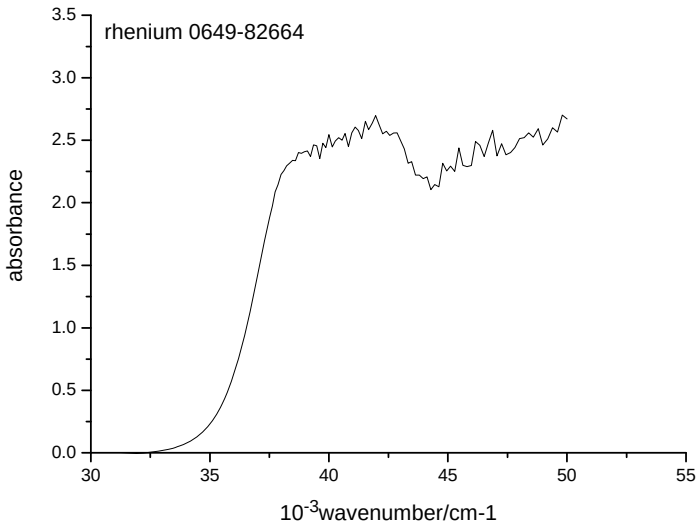


Figure 1 Uv spectra of rhenium REACH substances dissolved in deionised water.

The spectra are plotted superimposed in Figure 2.

A literature spectrum of potassium perrhenate is shown in Figure 3 constructed by digitising a photocopy of the original (A. Carrington, D. Schonland, M. C. R. Symons, J. Chem. Soc., 1957, 669).

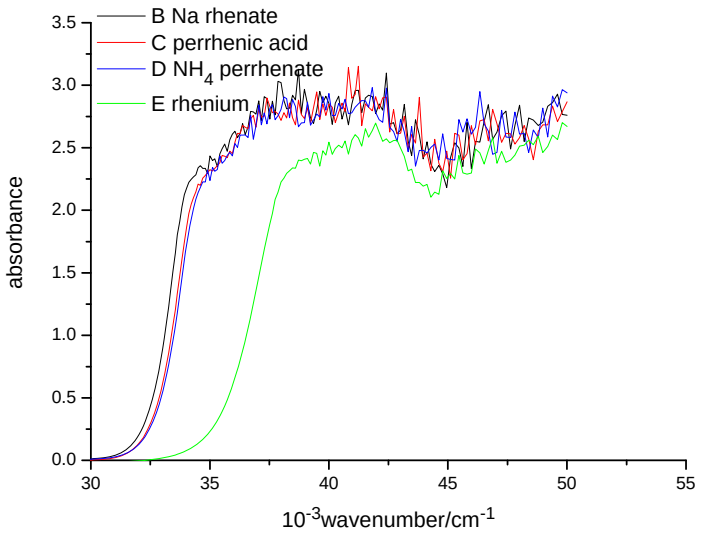


Figure 2 Uv spectra superimposed

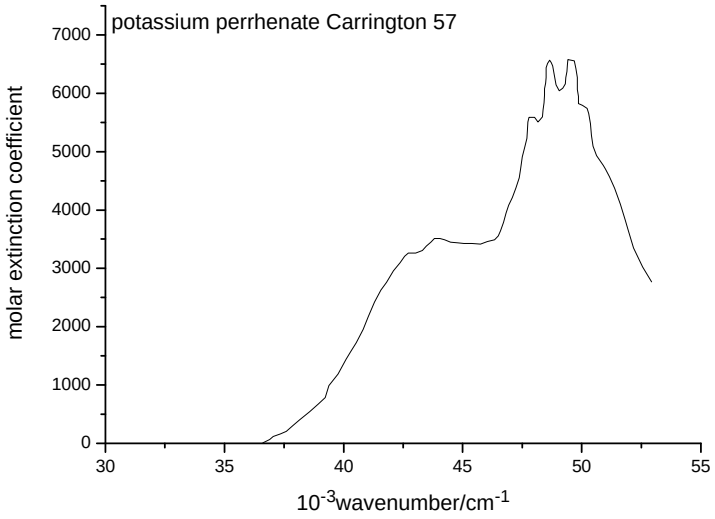


Figure 3 Literature spectrum of potassium perrhenate constructed by digitising a photocopy of the original (A. Carrington, D. Schonland, M. C. R. Symons, J. Chem. Soc., 1957, 669).

Concentrations and other data provided by Aqura are given in Table 1. I have calculated nominal rhenium concentrations and molar extinction coefficients using Beer's law

$A = \varepsilon cl$

Where A is the measured absorbance, ε is the molar extinction coefficient, c is concentration and l is path length. Customary units are c/mol L-1, l/cm (A is dimensionless).

Table 1 Perrhenate concentrations and uv absorbance								
		molar mass	g	ml	$molL^{-1}$	path/cm	absorbance	molar extinction /$1000mol^{-1} cm^2$
Na rhenate	$NaReO_4$	273.19	0.507	5.00	0.37	1.00	3.00	8.08
perrhenic acid	$HReO_4$	251.21	1.012	10.00	0.40	1.00	3.00	7.45
ammonium perrhenate	NH_4ReO_4	268.24	0.999	10.00	0.37	1.00	3.00	8.06
rhenium	Re	186.21	1.007	10.00	0.54	1.00	3.00	5.55

Comments

The spectra of sodium rhenate, perhenic acid and ammonium perrhenate are identical (Figure 2) showing that the dominant species in each solution is the same – presumably the $[ReO_4]^-$ ion. The spectrum from rhenium metal has the same general shape and peak position but with less absorbance at lower wavenumbers. We might tentatively conclude that the dominant species is also the $[ReO_4]^-$ ion. I suggest that perrhenate is formed by dissolution of a an oxide layer from rhenium metal in contact with water. There are however problems with the spectra which require our attention.

Problems and uncertainties

The difficulty is that the spectra reported by Aqura are broader and the peaks less resolved than for the literature spectrum (Figure 3). Such broadening of a uv spectrum is typically due to scattering by suspended particles. The solutions were prepared by dissolving substance in 5 or 10 ml volumes of water and not filtered – a procedure which might well provide some suspended matter. In agreement with this suggestion *we see a better resolved spectrum for the rhenium solution which was filtered.*

I have calculated the molar extinction coefficients (Table 1). They differ by a factor of 1000 from the literature value (6600) which may be a units problem. If we assume extinction coefficients of ca 8000 for the rhenium compounds then they have high values consistent with scattering from some suspended matter.

Conclusion

The uv spectra reported by Aqura are approximately similar for sodium rhenate, perrhenic acid, ammonium perrhenate and rhenium and the literature spectrum of the $[ReO_4]^-$ ion. We might tentatively conclude that the dominant species in the solutions is the perrhenate ion. However, the quality of the spectra is poor possibly because of the way in which the solutions were prepared giving some suspended matter. Colleagues might consider that the spectra should be re-measured with fresh, filtered solutions.