

Speciation of molybdenum compounds in water

Ultraviolet spectra and REACH read across

Report for the International Molybdenum Association

REACH Molybdenum Consortium

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Summary

The speciation of an element, speciation, is the distribution of an element amongst chemical species defined by composition and structure. For REACH we need to know whether substances in a biological environment yield the same or different species; whether one substance is representative of a group of substances; whether we can apply data from one representative substance to other related substances, a procedure known as read across.

For the purposes of REACH the molybdenum species produced in water when these substances are dissolved or stirred in suspension have been identified by ultraviolet spectroscopy of the water phase: sodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, ammonium dimolybdate, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, ammonium octamolybdate, $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26} \cdot 5\text{H}_2\text{O}$, calcium molybdate, CaMoO_4 , molybdenum metal powder, ferromolybdenum, molybdenum dioxide, MoO_2 , molybdenum trioxide, MoO_3 , roasted molybdenum concentrate (MoO_3), and molybdenum disulfide, MoS_2 . Species were identified by their characteristic uv spectra, peak positions and intensities. The spectra were analysed by decomposition into Gaussian peaks.

The uv spectral analysis has enabled us to describe the speciation in water solutions of soluble molybdates (sodium and ammonium molybdates) and in supernatant solutions of suspensions of poorly soluble molybdenum substances (calcium molybdate, molybdenum metal, ferromolybdenum, molybdenum dioxide, molybdenum trioxide, roasted molybdenum concentrate and molybdenum disulfide). The solutions and supernatant liquids contain the molybdate ion and, in addition at lower pHs, protonated molybdate. At biological concentrations and pH the only molybdenum species produced from the molybdenum substances studied is the molybdate, $[\text{MoO}_4]^{2-}$, ion. Read across from sodium molybdate is therefore justified.

The uv analysis provides the following results for each substance.

- ◆ Sodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$. In solution at concentrations 1–10 mgMo/L and pH 7 the molybdate ion, $[\text{MoO}_4]^{2-}$, is the only molybdenum species.
- ◆ Ammonium dimolybdate, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$. The molybdate species in solutions of ammonium dimolybdate is the $[\text{MoO}_4]^{2-}$ ion. There was some protonation of the molybdate ion as expected at pH 5.
- ◆ Ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. The molybdate species in solutions of ammonium heptamolybdate is the $[\text{MoO}_4]^{2-}$ ion. There was some protonation of the molybdate ion as expected at pH 5.
- ◆ Ammonium octamolybdate, $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26} \cdot 5\text{H}_2\text{O}$. The molybdate species in solutions of ammonium octamolybdate are $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$, and $[\text{H}_2\text{MoO}_4]$ consistent with pH 3.3
- ◆ Calcium molybdate CaMoO_4 . The molybdate species in solutions of calcium molybdate are $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$, and $[\text{H}_2\text{MoO}_4]$ consistent with pH 4.
- ◆ Molybdenum metal powder. Molybdenum metal powder suspended in water for 24 h produces a water phase (supernatant) containing only the $[\text{MoO}_4]^{2-}$ ion. Molybdate is formed by dissolution of a surface layer of MoO_3 . There is no evidence of other molybdenum species.

- ♦ Ferromolybdenum. Ferromolybdenum suspended in water produces a water phase (supernatant) containing only the $[\text{MoO}_4]^{2-}$ ion. Molybdate is formed by dissolution of a surface layer of MoO_3 . There is a background of ca 10% which may be due to iron.
- ♦ Molybdenum dioxide, MoO_2 . Molybdenum dioxide suspended in water produces a water phase (supernatant) containing the $[\text{HMoO}_4]^-$ and $[\text{H}_2\text{MoO}_4]$ formed by dissolution of a surface layer of MoO_3 at pH 3.6. Lower valent molybdenum species are absent.
- ♦ Molybdenum trioxide, MoO_3 . Molybdenum dioxide suspended in water produces a water phase (supernatant) containing $[\text{H}_2\text{MoO}_4]$ and $[\text{Mo}_7\text{O}_{24}]^{6-}$. The heptamolybdate represents less than 10% of the total molybdenum; its presence is due to the low pH (2.2) and the molybdenum concentration (ca 0.6mM).
- ♦ Roasted molybdenum concentrate. The supernatant solution from roasted molybdenum concentrate suspended in water has a uv spectrum similar to the spectrum of MoO_3 showing evidence for $[\text{H}_2\text{MoO}_4]$ and $[\text{Mo}_7\text{O}_{24}]^{6-}$. The heptamolybdate represents ca 20% of the total molybdenum; its presence is due to the low pH (2.6) and the molybdenum concentration (ca 0.7mM).
- ♦ Molybdenum disulfide. Molybdenum disulfide suspended in water produces a water phase (supernatant) containing $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$ and $[\text{H}_2\text{MoO}_4]$. They are formed by dissolution of a surface layer of MoO_3 at pH 4.5.

The spectra were measured by the Fraunhofer Institute for Molecular Biology and Applied Ecology, Division Applied Ecology, Schmallenberg, Germany and analysed and interpreted by the author of this Report.

Speciation

The speciation of an element, speciation, is the distribution of an element amongst chemical species defined by composition and structure. For REACH we need to know whether substances in a biological environment yield the same or different species; whether one substance is representative of a group of substances; whether we can apply data from one representative substance to other related substances, a procedure known as read across.

Uv spectra

The ultraviolet (uv) spectra of molybdenum compounds dissolved in water or stirred in suspension in water have been measured in order to identify the molybdenum species in solution (the speciation). Particular species may be identified by the positions and intensities of peaks in the uv spectra. The spectra were measured by the Fraunhofer Institute for Molecular Biology and Applied Ecology, Division Applied Ecology, Schmallenberg, Germany. The compounds studied were sodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, ammonium dimolybdate, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, ammonium octamolybdate, $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26} \cdot 5\text{H}_2\text{O}$, molybdenum metal powder, molybdenum dioxide, MoO_2 , molybdenum trioxide, MoO_3 , roasted molybdenum concentrate (MoO_3), and molybdenum disulfide, MoS_2 . Molybdate species in solution were identified by comparison with the literature. The species in solutions of sodium molybdate at concentrations 1–10 mg/L and pH ca 7 is the the molybdate ion, $[\text{MoO}_4]^{2-}$ with a uv absorption maximum (peak) at 207–208 nm (48000 cm^{-1}). As the pH is lowered the $[\text{MoO}_4]^{2-}$ ion becomes protonated giving $[\text{HMoO}_4]^-$ and $[\text{H}_2\text{MoO}_4]$ species, the peaks in the uv spectra shifting to lower energies (longer wavelengths). From our uv-spectra we shall see that the predominant (>90%) species from our compounds in solution or in contact with water are the $[\text{MoO}_4]^{2-}$ and $[\text{HMoO}_4]^-$ ions. The uv spectral analysis has enabled us to describe the speciation in water solutions of soluble molybdates (sodium and ammonium molybdates) and in supernatant solutions of suspensions of poorly soluble molybdenum substances (calcium molybdate, molybdenum metal, ferromolybdenum, molybdenum dioxide, molybdenum trioxide,

roasted molybdenum concentrate and molybdenum disulfide). The solutions and supernatant liquids contain the molybdate ion and, in addition at lower pHs, protonated molybdate. At biological concentrations and pH the only molybdenum species produced from the molybdenum substances studied is the molybdate, $[\text{MoO}_4]^{2-}$, ion. Read across from sodium molybdate is therefore justified.

Uv spectra of molybdates—purpose of the study: speciation and read across

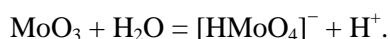
The purpose of the study was to identify the molybdenum species in solution when molybdenum compounds are dissolved in or contacted with water. The bioavailability of molybdenum—how much molybdenum is released into water and in what form (as molybdate or as some other species)—is fundamental to our understanding the impact of molybdenum on human health and the environment. Knowing the speciation of molybdenum (the chemical nature of the species in solution) is needed in consideration of the feasibility of read across in the REACH classification of our molybdenum compounds, i.e. whether all of the compounds studied release the same molybdenum species into the environment or whether each compound is unique. We chose sodium molybdate for our biological testing. Sodium molybdate yields $[\text{MoO}_4]^{2-}$ ions in water and, therefore, the species applied in our biological tests is the $[\text{MoO}_4]^{2-}$ ion. The question then is whether our other REACH compounds yield the $[\text{MoO}_4]^{2-}$ ion in water. If they do yield solutions having $[\text{MoO}_4]^{2-}$ as the only (or dominant) species (and we shall see that they do) then we can assume that they will have the same biological effect as molybdate: we can read across from molybdate to our other compounds. We shall see that the compounds under study for REACH all behave in a similar manner with water, releasing molybdate, and so can be grouped together for classification purposes.

Molybdenum substances for REACH

The molybdenum substances being submitted for REACH classification by the IMOIA Molybdenum Consortium are: sodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, ammonium dimolybdate, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, ammonium octamolybdate, $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26} \cdot 6\text{H}_2\text{O}$, calcium molybdate, CaMoO_4 , molybdenum metal powder, molybdenum dioxide, MoO_2 , molybdenum trioxide, MoO_3 , and roasted molybdenum concentrate (MoO_3). Molybdenum disulfide, MoS_2 , was also included in the study.

Dissolution of the REACH compounds in water and bioavailability

The interaction of these compounds with water is fundamental to our understanding how they contribute to the bioavailability of molybdenum. The release of molybdenum into solution has loosely been referred to as solubility although strictly we should think of the behaviour with water as a chemical reaction. For example with molybdenum trioxide



The surface of MoO_3 particles reacts with water; molybdenum–oxygen bonds are broken; and the molybdate ion appears in solution. The species in solution is molybdate, never molybdenum trioxide. The dissolution reaction generates protons which is why the water in contact with MoO_3 is acidic.

Equilibria of molybdate species in water

Uv spectra provide a means of estimating the fractions of molybdate species in solution as a function of total molybdenum concentration and pH, see Figure 1 (T. Ozeki, H. Kihara, and S. Ikeda *Anal. Chem.*, 1988, 60 (19), 2055-2059: Study of equilibria in 0.03 mM molybdate acidic aqueous solutions by factor analysis applied to ultraviolet spectra). From this graph we can estimate the species in solutions of our REACH compounds. For a concentration below 10 mg Mo/L (10 ppm, approx 0.1 mmole Mo/L (0.1mM Mo)) we expect the speciation to be as in Figure 1C with the $[\text{MoO}_4]^{2-}$ ion as the only species above pH 5.5.

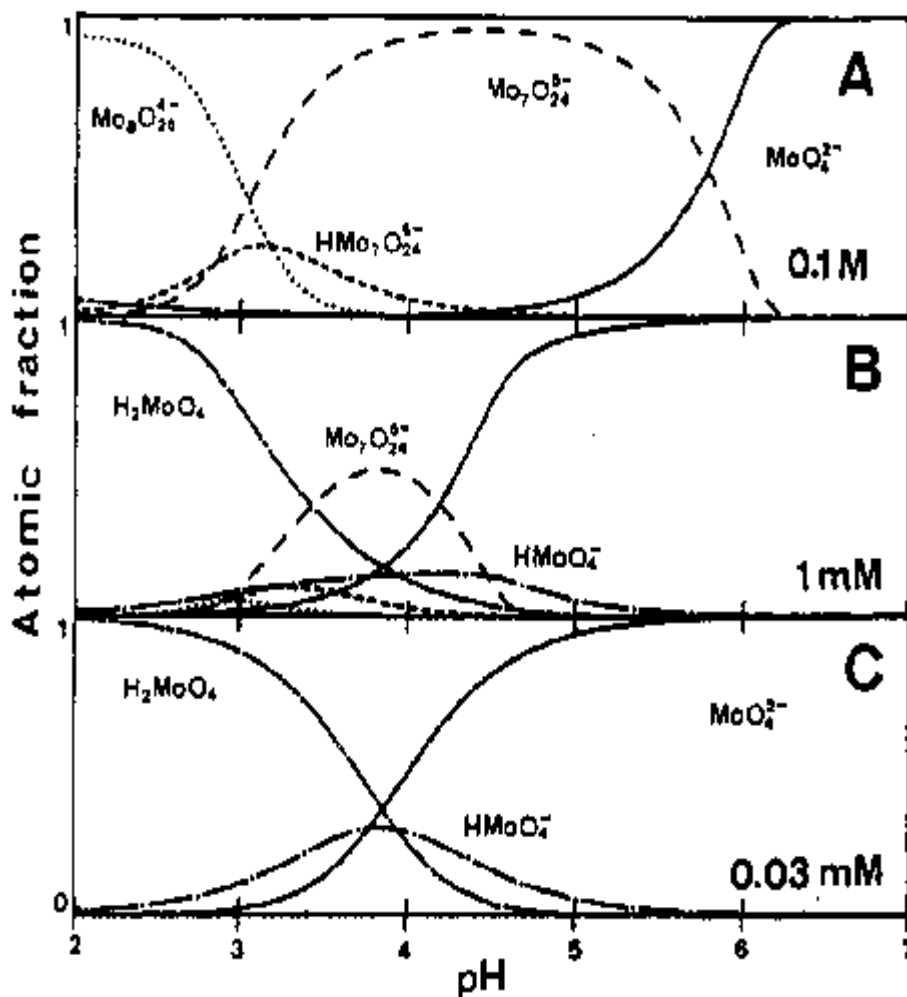


Figure 1. Distribution diagram for molybdate species in water determined by uv spectroscopy. Total molybdate concentrations: A, 0.1 M (ca 10 gMo/L); B, 1 mM (ca 0.1 gMo/L); C 0.03 mM (ca 3 mgMo/L) (T. Ozeki, H. Kihara, and S. Ikeda *Anal. Chem.*, 1988, 60 (19), 2055).

Determination of solubilities and uv spectra

The solubility of our molybdenum compounds in water and the uv spectra of the solutions have been determined at the Fraunhofer Institute for Molecular Biology and Applied Ecology, Division Applied Ecology, Schmallenberg, Germany. The uv spectra of the solutions were measured to identify the molybdenum species in solution. Experimental methods are described in the Fraunhofer report.

Technical background —reference uv spectra

We interpret our spectra by comparing them with the spectra of known species, our reference spectra. Reference spectra are in the literature and from measurements which I or my students made in the 1960s. (P. C. H. Mitchell, *Quart. Rev.*, 1966, 20, 103; J. H. Ashley and P. C. H. Mitchell, *J. Chem. Soc. (A)*, 1968, 2821; J. H. Ashley and P. C. H. Mitchell, *J. Chem. Soc. (A)* 1969, 2730; P. C. H. Mitchell and F. Trifiro, *J. Chem. Soc. (A)*, 1970, 3183; A.W. Armour, PhD Thesis, Reading 1972). I have the spectra of solid powders of sodium molybdate, sodium dimolybdate, ammonium heptamolybdate, and molybdenum trioxide. The structures of the solids are known from X-ray crystallography and contain molybdenum species of known structure. They can be used as reference spectra for particular structures if we assume that solid state and solution spectra of the same species are similar. The key point is that molybdate $[\text{MoO}_4]^{2-}$ is tetrahedral whereas the polymolybdates and molybdenum trioxide are octahedral. The uv spectra are, as we shall see different, the octahedral structures having additional and broader peaks to longer wavelengths compared with the tetrahedral structure. Reference spectra are shown in Figures 2 and 3.

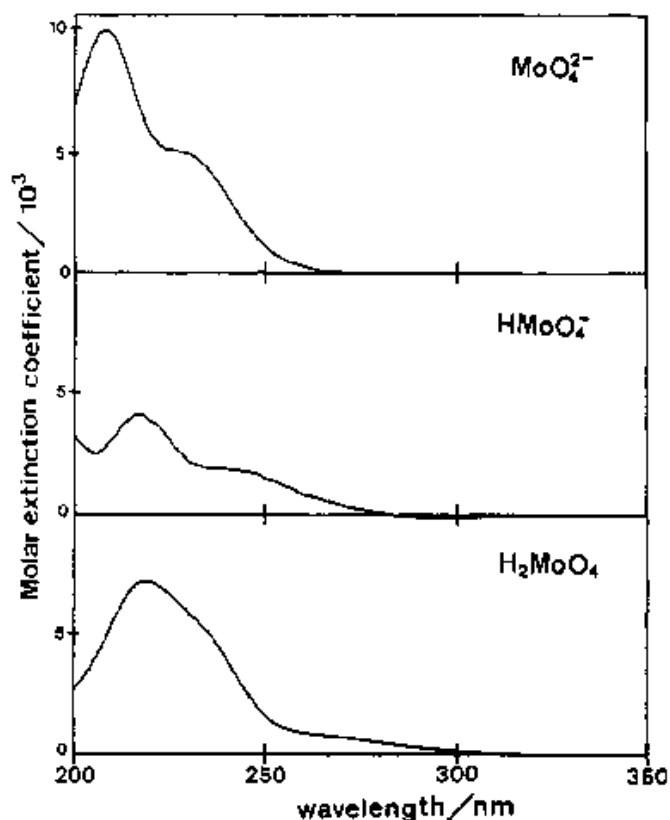


Figure 2. Uv spectra of $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$, and $[\text{H}_2\text{MoO}_4]$ Peak positions and intensities are in Table 1. Note how protonation shifts and broadens the peaks to longer wavelengths. (T. Ozeki, H. Kihara, and S. Ikeda *Anal. Chem.*, 1988, 60 (19), 2055).

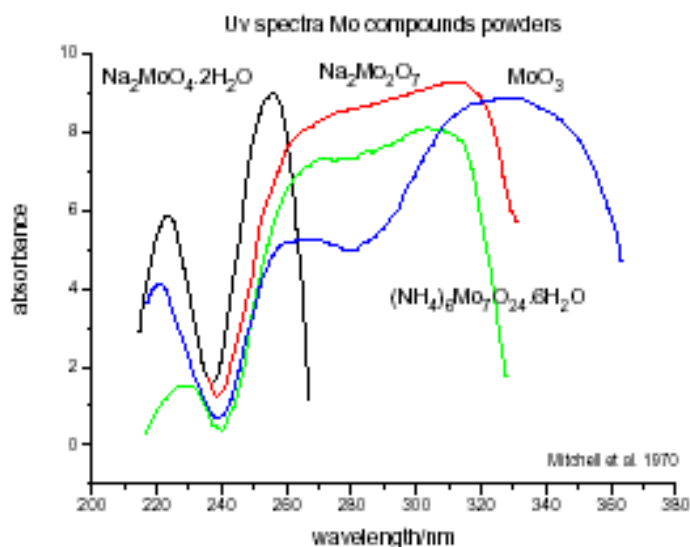


Figure 3. Uv spectra of solid molybdenum compounds. Note how the peaks are shifted to longer wavelengths in polymolybdates and MoO_3 compared to sodium molybdate.

Analysis of the uv spectra of our REACH compounds

The Fraunhofer Institute supplied the spectra as Excel data files of wavelengths and intensities which I have analysed and interpreted. The spectra consist of overlapping peaks which I have analysed into Gaussian peaks. For the Gaussian analysis it is necessary to plot the spectra in energy units (cm^{-1}) since it is the energies which are Gaussian functions. On the spectra the colour coding is: black trace, measured spectrum, green, gaussians, red summed gaussians regenerating the measured spectrum. The precision is ca $\pm 1\%$.

Presentation of results

Our aims are

- ◆ To determine the molybdate species in aqueous solutions derived from our compounds
- ◆ To assess the validity of read across from sodium molybdate for each compound.

The results for each compound are presented with reference to these two aims.

Sodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$

The spectra

Our spectra of sodium molybdate solutions are in Figure 4.

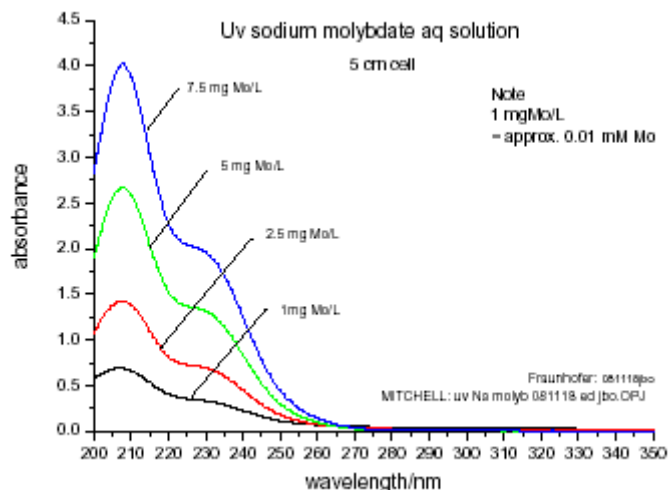


Figure 4. Uv spectra (absorbance vs wavelength) of sodium molybdate solutions of concentrations 1–7.5 mg/L and pH 7. (The 10 mg solution was measured in a 1 cm cell and is not on this graph.) .

Our sodium molybdate spectra are identical with the literature spectrum, having a peak at 207–208 nm and a shoulder near 232 nm (see Figure 2). In Figure 5 one of the sodium molybdate spectra is shown decomposed into Gaussian peaks and compared with a literature spectrum (Ozeki) which I have re-drawn. Peak positions and intensities are compared in Table 1. The spectra are identical.

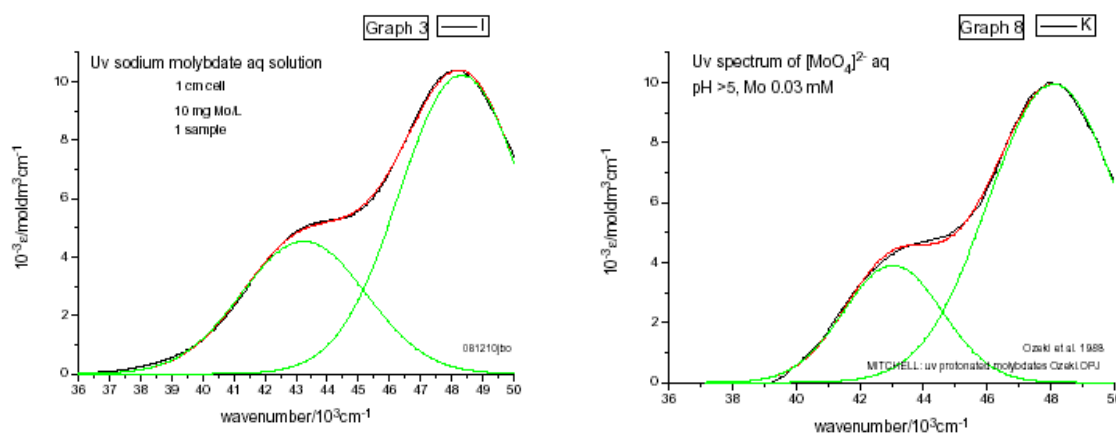


Figure 5. Sodium molybdate solution spectra: our spectrum (left) and the literature spectrum redrawn from Ozeki et al. (right). The vertical scale is the molar extinction coefficient.

Table 1. Uv spectra of sodium molybdate from the IMOA REACH studies and the literature spectrum of the $[\text{MoO}_4]^{2-}$ ion		
	REACH sodium molybdate	$[\text{MoO}_4]^{2-}$ ion
Peak I/ 10^3cm^{-1}	48.3	48.1
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$	10.2	9.9
Peak II/ 10^3cm^{-1}	43.2	43.0
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$	4.5	3.9

Concentration dependence

The form of our spectra (peak position and shape) does not change with concentration: the same species, the $[\text{MoO}_4]^{2-}$ ion is present at all concentrations. This is confirmed by the Beer's law plot below. The concentration dependence of our sodium molybdate spectra is shown in Figure 6. This is a Beer's law plot.

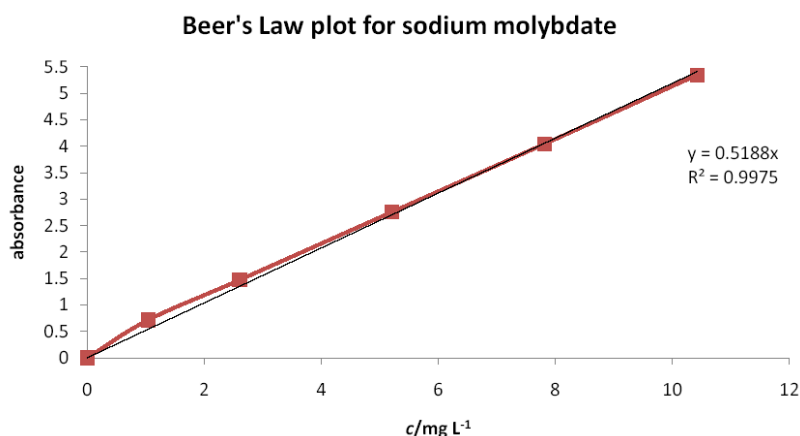


Figure 6. Beer's law plot for sodium molybdate solutions.

Uv absorbance of the 207 nm ($48\,000\text{cm}^{-1}$) peak is plotted vs concentration of molybdenum. The plot is strictly linear through the origin over the concentration range measured. The linearity shows that there is only one molybdenum species in the solution, the $[\text{MoO}_4]^{2-}$ ion. If molybdate was, for example, polymerising to heptamolybdate or octamolybdate so setting up chemical equilibria which were a function of molybdenum concentration, then the concentration of the molybdate ion would not vary in a linear manner with the total molybdenum and the Beer's law plot would not be linear. This result is in accordance with all that is known about molybdate solutions: at pH 7 and molybdenum concentrations below 10^{-4}M the molybdenum species is the $[\text{MoO}_4]^{2-}$ ion.

pH dependence of molybdate spectra

The molybdate uv spectra change as the pH is lowered (not studied here), see Figure 7. The spectra (re-drawn from Ozeki) are shown here to enable comparison with the spectra of solutions of low pH and peaks are listed in Table 2.

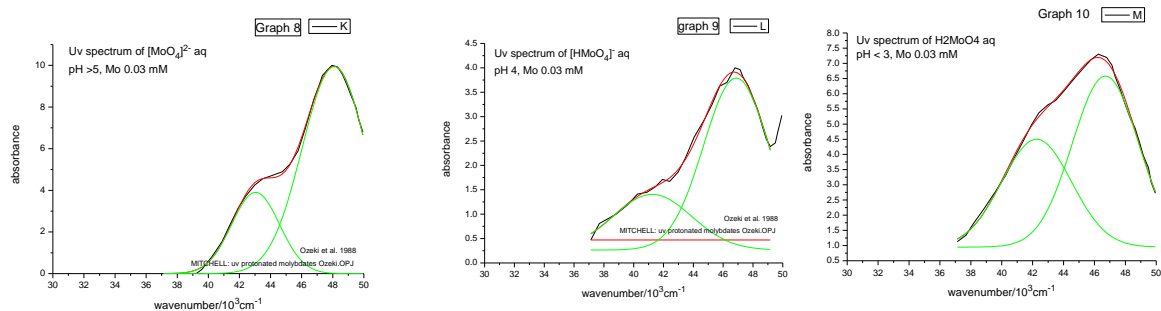


Figure 7. Spectra of the species , $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$, and $[\text{H}_2\text{MoO}_4]$.

Table2. Uv spectra of molybdate and protonated molybdates			
	$[\text{MoO}_4]^{2-}$ ion	$[\text{HMoO}_4]^-$	$[\text{H}_2\text{MoO}_4]$
pH	pH 7.0	pH 4	pH <3
Peak I/ 10^3cm^{-1}	48.1	46.9	46.7
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$	9.9	3.5	5.6
Peak II/ 10^3cm^{-1}	43.0	41.3	42.2
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$	3.9	1.1	3.6

Conclusion

The molybdate species in solutions of our REACH sodium molybdate is the $[\text{MoO}_4]^{2-}$ ion.

Ammonium dimolybdate, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$.

The spectrum compared with sodium molybdate is in Figure 8.

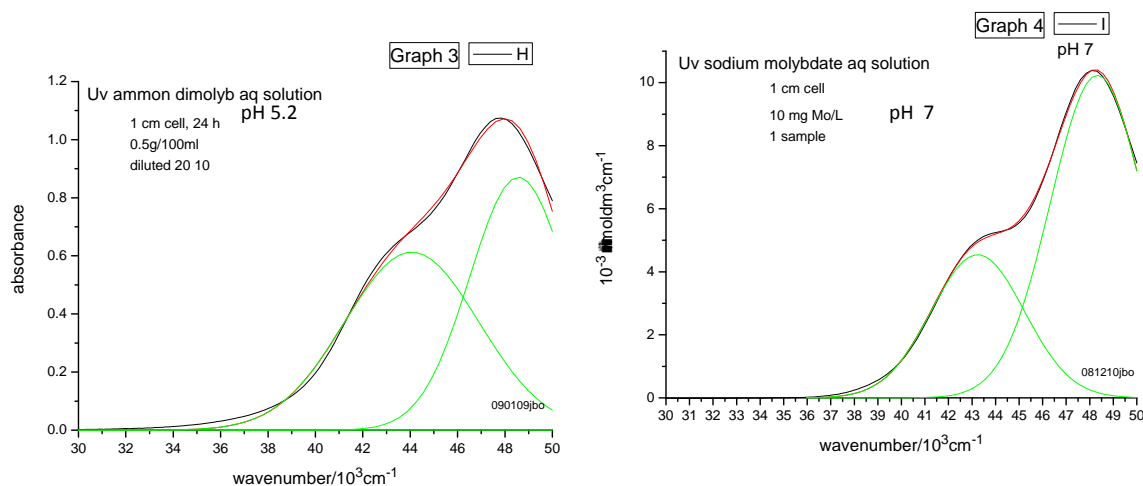


Figure 8. Ammonium dimolybdate (left) and sodium molybdate (right) solution spectra.

Table 3. Uv spectra of ammonium dimolybdate and sodium molybdate from the IMO A REACH studies		
	Ammonium dimolybdate	REACH sodium molybdate
Peak I/ 10^3cm^{-1}	48.6	48.3
absorbance	0.87	
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		10.2
Peak II/ 10^3cm^{-1}	44.1	43.2
Absorbance	0.61	
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		4.5

Conclusion

The molybdate species in solutions of ammonium dimolybdate is the $[\text{MoO}_4]^{2-}$ ion. Two peaks gave the best fit but the relative increase of intensity of peak II indicates some protonation of the molybdate ion (cf. Figure 7 above and Table 3) as expected at pH 5.

Ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$

The spectrum compared with sodium molybdate is in Figure 9 and the peaks in Table 4.

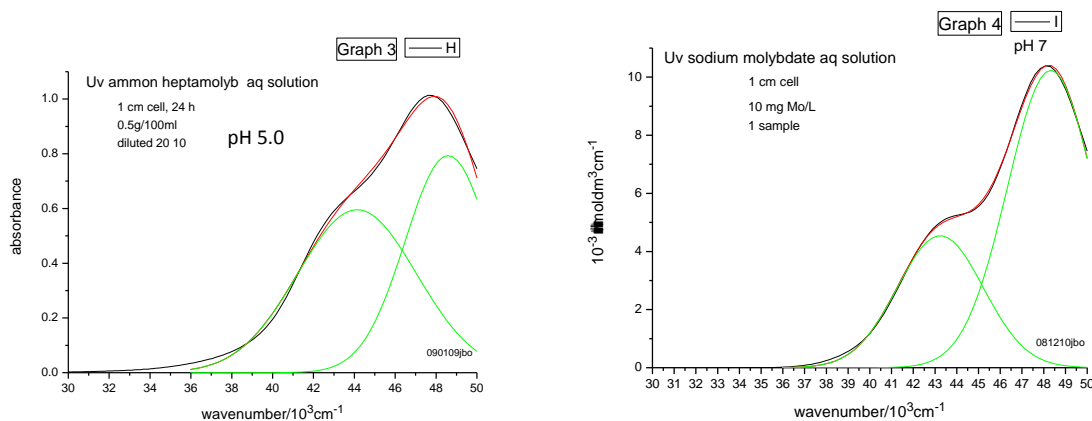


Figure 9. Uv spectra of ammonium heptamolybdate and sodium molybdate.

Table 4. Uv spectra of ammonium heptamolybdate and sodium molybdate from the IMO A REACH studies		
	Ammonium heptamolybdate	REACH sodium molybdate
Peak I/ 10^3cm^{-1}	48.6	48.3
absorbance	0.79	
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		10.2
Peak II/ 10^3cm^{-1}	44.1	43.2
Absorbance	0.60	
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		4.5

Conclusion

The molybdate species in solutions of ammonium heptamolybdate is the $[\text{MoO}_4]^{2-}$ ion. Two peaks gave the best fit but the relative increase of intensity of peak II indicates some protonation of the molybdate ion (cf. Figure 7) as expected at pH 5.

Ammonium octamolybdate, $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26}\cdot 5\text{H}_2\text{O}$

The spectrum compared with sodium molybdate is in Figure 9 and the peaks in Table 5

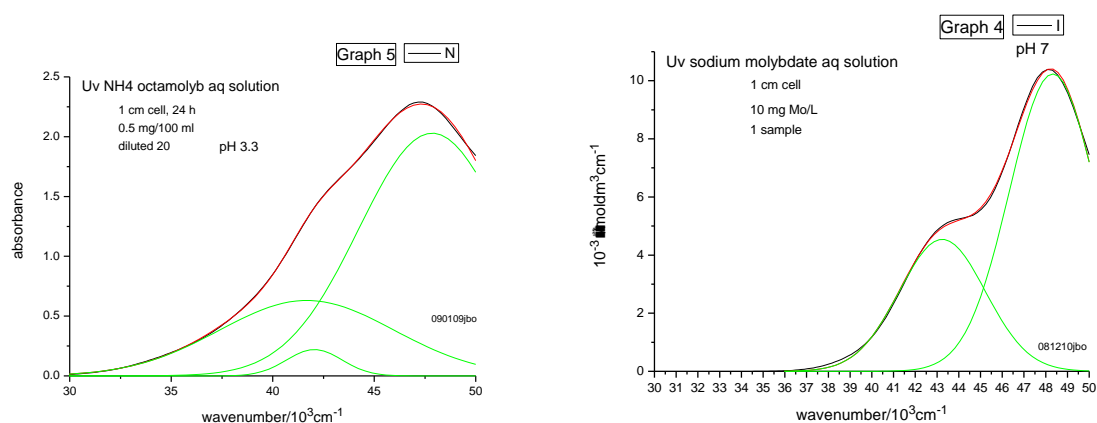


Figure 10. Uv spectra of ammonium octamolybdate and sodium molybdate

Table 5. Uv spectra of ammonium octamolybdate and sodium molybdate from the IMO A REACH studies				
	Ammonium octamolybdate	REACH sodium molybdate	$[\text{HMoO}_4]^-$	$[\text{H}_2\text{MoO}_4]$
	pH 3.3	pH 7	pH 4	pH <3
Peak I/ 10^3cm^{-1}	47.9	48.3	46.9	46.7
absorbance	2.03			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		10.2	3.5	5.6
Peak II/ 10^3cm^{-1}	42.1	43.2		42.2
Absorbance	0.22			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		4.5		3.6
Peak III/ 10^3cm^{-1}	41.7		41.3	
Absorbance	0.63			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$			1.1	

Conclusion

The uv spectrum of ammonium octamolybdate is noticeably broadened compared with sodium molybdate. Three peaks can be fitted. They are listed in Table 5 and correlated with peaks in the spectra of molybdate and protonated molybdate (bold). The molybdate species in solutions of ammonium octamolybdate are $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$, and $[\text{H}_2\text{MoO}_4]$ consistent with pH 3.3 (see Figure 1).

Calcium molybdate CaMoO_4

The spectrum compared with sodium molybdate is in Figure 11 and the peaks in Table 6.

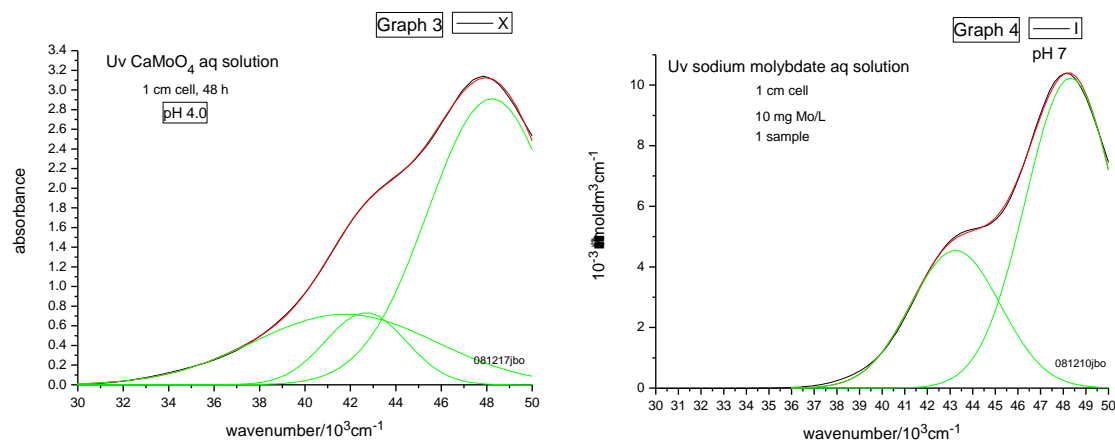


Figure 11. Uv spectra of calcium molybdate and sodium molybdate.

Table 6. Uv spectra of calcium molybdate and sodium molybdate from the IMOA REACH studies				
	Calcium molybdate	REACH sodium molybdate	$[\text{HMoO}_4]^-$	$[\text{H}_2\text{MoO}_4]$
	pH 4	pH 7	pH 4	pH <3
Peak I/ 10^3cm^{-1}	48.2	48.3	46.9	46.7
absorbance	2.9			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		10.2	3.5	5.6
Peak II/ 10^3cm^{-1}	42.6	43.2		42.2
Absorbance	0.72			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		4.5		3.6
Peak III/ 10^3cm^{-1}	41.7		41.3	
Absorbance	0.72			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$			1.1	

Conclusion

The uv spectrum of calcium molybdate is noticeably broadened compared with sodium molybdate. Three peaks can be fitted. They are listed in Table 6 and correlated with peaks in the spectra of

molybdate and protonated molybdate (bold). The molybdate species in solutions of calcium molybdate are $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$, and $[\text{H}_2\text{MoO}_4]$ consistent with pH 4 (see Figure 1).

Molybdenum metal powder.

The powder was stirred with water. Spectra were recorded at intervals between 0.5 and 192h. The pH of the solution was 4.5–5.0. The spectrum recorded after 0.5 h is typical and is compared with sodium molybdate in Figure 12 and the peaks in Table 7

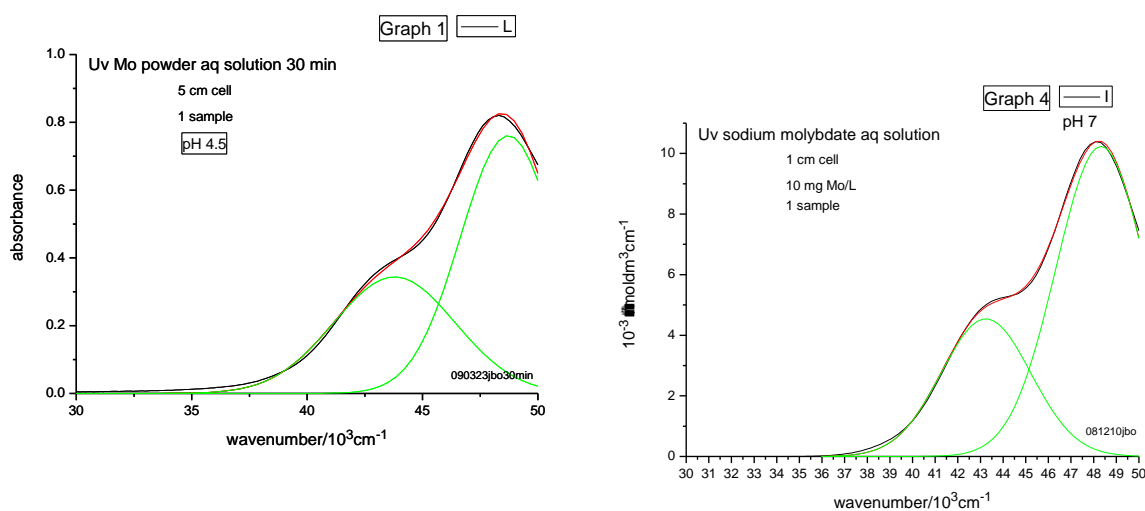


Figure 12. Uv spectra of molybdenum metal powder and sodium molybdate.

Table 7. Uv spectra of molybdenum metal powder and sodium molybdate from the IMO REACH studies		
	Mo metal powder 30 min	REACH sodium molybdate
pH	4.5-5.0	7.0
Peak I/ 10^3cm^{-1}	48.7	48.3
absorbance	0.76	
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		10.2
Peak II/ 10^3cm^{-1}	43.8	43.2
Absorbance	0.34	
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		4.5

Comment

The spectrum of the water phase in contact with molybdenum metal powder is very similar to the spectrum of sodium molybdate. The ratios of the absorbances peak I/peak II are: for molybdenum

powder 2.21 and sodium molybdate 2.25 confirming that the species in the solution derived from molybdenum powder is the $[\text{MoO}_4]^{2-}$ ion. There were no peaks in the region below 30000 cm^{-1} ; therefore lower valent molybdenum (which is coloured) was absent. A reasonable interpretation that the molybdenum in solution derives from dissolution of a surface layer of molybdenum trioxide. This would account for the lowering of the pH (to ca 5).

How the spectrum varies with time is shown in Figure 13. There are two processes. The first is complete after ca 6 h; this is the dissolution of surface MoO_3 .

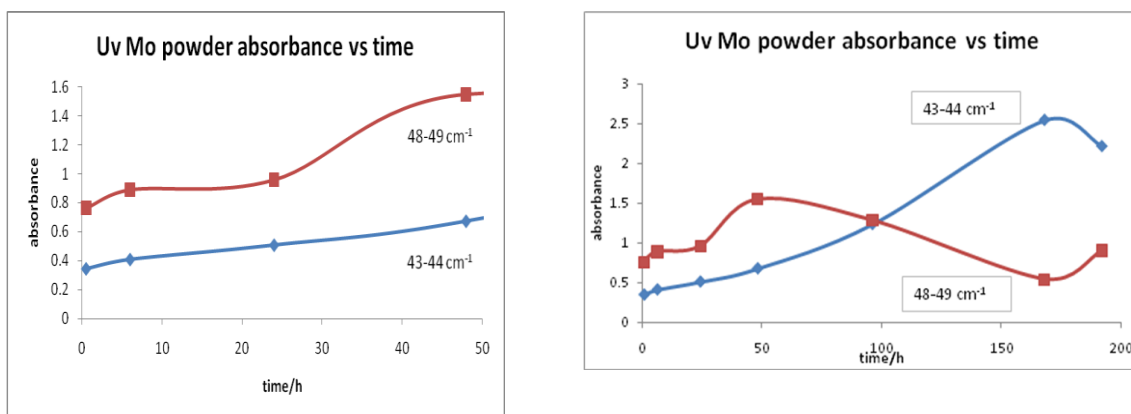


Figure 13. Change with time of contact of the uv spectrum of the water phase from molybdenum metal powder.

Conclusion

When molybdenum metal powder is in contact with water for 24 h the water phase contains only the $[\text{MoO}_4]^{2-}$ ion which is formed by dissolution of a surface layer of MoO_3 . There is no evidence of the formation of other molybdenum species.

Ferromolybdenum

The spectrum compared with sodium molybdate is in Figure 14 and the peaks in Table 8.

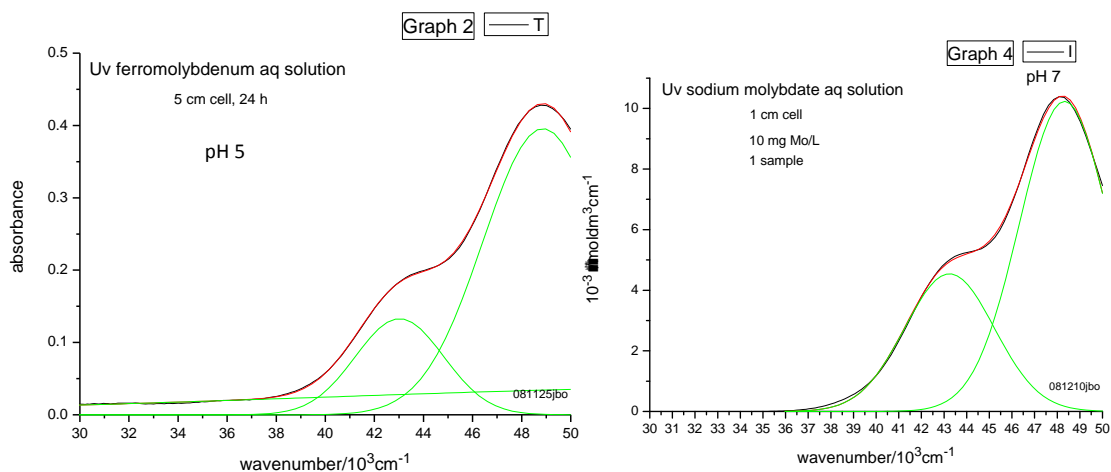


Figure 14. Uv spectra of ferromolybdenum and sodium molybdate

Table 8. Uv spectra of ferromolybdenum and sodium molybdate from the IMO A REACH studies		
	Ferromolybdenum	REACH sodium molybdate
pH	5.0	7.0
Peak I/ 10^3cm^{-1}	48.8	48.3
absorbance $\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$	0.40	10.2
Peak II/ 10^3cm^{-1}	43.0	43.2
Absorbance $\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$	0.13	4.5

Conclusion

The uv spectrum of the water phase from ferromolybdenum in contact with water shows that the major species is the $[\text{MoO}_4]^{2-}$ ion. There is a background of ca 10% which may be due to iron.

Molybdenum dioxide, MoO₂

The spectrum compared with sodium molybdate is shown in Figure 15 and the peaks in Table 9.

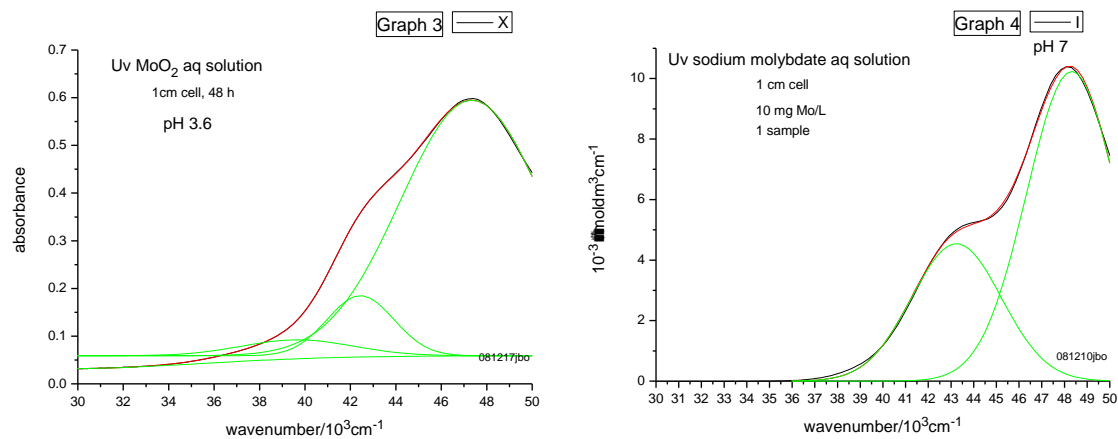


Figure 15. Uv spectra of molybdenum dioxide and sodium molybdate.

Comment

The spectrum is broadened compared with sodium molybdate. This is due to protonation of molybdate, see Table 8. The most likely species in the solution are $[\text{HMoO}_4]^-$ and $[\text{H}_2\text{MoO}_4]$ formed by dissolution of a surface layer of MoO_3 at pH 3.6.

Table 8. Uv spectra of molybdenum dioxide and sodium molybdate from the IMOA REACH studies				
	Molybdenum dioxide	REACH sodium molybdate	$[\text{HMoO}_4]^-$	$[\text{H}_2\text{MoO}_4]$
	pH 3.6	pH 7	pH 4	pH <3
Peak I/ 10^3cm^{-1}	47.4	48.3	46.9	46.7
absorbance	0.55			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		10.2	3.5	5.6
Peak II/ 10^3cm^{-1}	42.4	43.2		42.2
Absorbance	0.12			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		4.5		3.6
Peak III/ 10^3cm^{-1}	40.4		41.3	
Absorbance	0.057			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$			1.1	

Conclusion

The uv spectrum of the water phase from molybdenum dioxide in contact with water shows that the major species are $[\text{HMoO}_4]^-$ and $[\text{H}_2\text{MoO}_4]$ formed by dissolution of a surface layer of MoO_3 at pH 3.6. The solution is colourless: there is no absorbance in the visible region and so lower valent molybdenum species (which are coloured) are absent.

Molybdenum trioxide, MoO₃.

The uv spectrum is compared with sodium molybdate in Figure 16 and peaks are in Table 9.

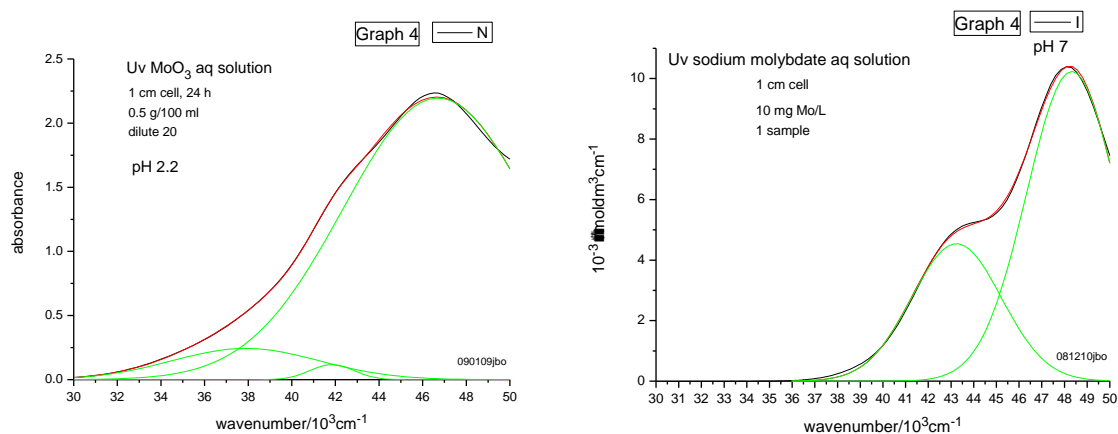


Figure 16. Uv spectra of water solution from molybdenum trioxide and sodium molybdate.

Table 9. Uv spectra of molybdenum trioxide and sodium molybdate from the IMO A REACH studies					
	Molybdenum trioxide	REACH sodium molybdate	[HMoO ₄] ⁻	[H ₂ MoO ₄]	[Mo ₇ O ₂₄] ⁶⁻ ^a
	pH 2.2	pH 7	pH 4	pH <3	pH 4 1mM Mo
Peak I/10 ³ cm ⁻¹	46.6	48.3	46.9	46.7	
absorbance ε/10 ³ molModm ³ cm ⁻¹	2.19	10.2	3.5	5.6	
Peak II/10 ³ cm ⁻¹	41.8	43.2		42.2	
Absorbance ε/10 ³ molModm ³ cm ⁻¹	0.12	4.5		3.6	
Peak III/10 ³ cm ⁻¹	37.8		41.3		38.8
Absorbance ε/10 ³ molModm ³ cm ⁻¹	0.24		1.1		

^a For spectrum of ammonium heptamolybdate see: Erno Pungor And Andras Halasz, J. Inorg. Nucl. Chem., 1970, 32.1187 - 1197: Spectrophotometric Examination Of The Isopolyacide Of Molybdenum.

Comment

The uv spectrum of the supernatant solution from MoO_3 is much broadened compared with sodium molybdate. The peak analysis shows a peak at ca 38000 cm^{-1} . This peak is not assigned to molybdate or protonated molybdate but can be assigned to heptamolybdate (see Table). From the uv absorbance I estimate a molybdenum concentration of ca 0.6 mM . With this concentration and pH 2.2 we expect some heptamolybdate (see Figure 1, if we extend the heptamolybdate to the lower pH region), less than 10% of the total molybdenum. See also Figure 3 for the uv spectrum of solid ammonium heptamolybdate ($37800\text{ cm}^{-1} = 264\text{ nm}$) showing a peak at ca 270 nm .

Conclusion

The uv spectrum of the supernatant solution from MoO_3 shows evidence for $[\text{H}_2\text{MoO}_4]$ and $[\text{Mo}_7\text{O}_{24}]^{6-}$. The heptamolybdate represents less than 10% of the total molybdenum; its presence is due to the low pH (2.2) and the molybdenum concentration (ca 0.6 mM).

Roasted molybdenum concentrate

The spectrum is similar to that of MoO_3 but broader, see Figure 17. Peaks are given in Table 10.

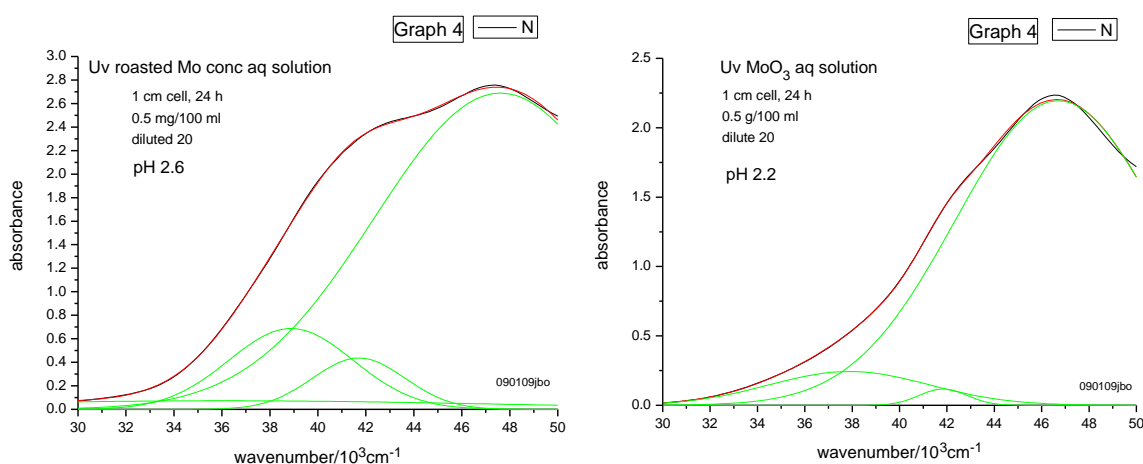


Figure 17. Uv spectra of roasted molybdenum concentrate and MoO_3 .

Comment

The uv spectrum of the supernatant solution from roasted molybdenum concentrate is like MoO_3 much broadened compared with sodium molybdate. The peak analysis shows a peak at ca 38000 cm^{-1} . This peak is not assigned to molybdate or protonated molybdate but can be assigned to heptamolybdate (see Table). See also Figure 3 for the uv spectrum of solid ammonium heptamolybdate ($37800\text{ cm}^{-1} = 264\text{ nm}$) showing a peak at ca 270 nm . From the uv absorbance I estimate a molybdenum concentration of ca 0.7 mM (cf. 0.6 molybdenum from MoO_3). With this concentration and pH 2.6 we expect some heptamolybdate (see Figure 1, if we extend the heptamolybdate to the lower pH region), rather more than for MoO_3 (by a factor of 2–3 to judge from the absorbances (Table 9)).

Table 10. Uv spectra of roasted molybdenum concentrate and molybdenum trioxide and sodium molybdate from the IMOA REACH studies						
	Roasted molybdenum concentrate	Molybdenum trioxide	REACH sodium molybdate	[HMoO ₄] ⁻	[H ₂ MoO ₄]	[Mo ₇ O ₂₄] ⁶⁻ ^a
	pH 2.6	pH 2.2	pH 7	pH 4	pH <3	pH 4 1mM Mo
Peak I/10 ³ cm ⁻¹	47.6	46.6	48.3	46.9	46.7	
absorbance ε/10 ³ molModm ³ cm ⁻¹	2.7	2.19	10.2	3.5	5.6	
Peak II/10 ³ cm ⁻¹	41.7	41.8	43.2		42.2	
Absorbance ε/10 ³ molModm ³ cm ⁻¹	0.44	0.12	4.5		3.6	
Peak III/10 ³ cm ⁻¹	38.8	37.8		41.3		38.8
Absorbance ε/10 ³ molModm ³ cm ⁻¹	0.68	0.24		1.1		

Conclusion

The uv spectrum of the supernatant solution from roasted molybdenum concentrate is similar to the spectrum of MoO₃ showing evidence for [H₂MoO₄] and [Mo₇O₂₄]⁶⁻. The heptamolybdate represents ca 20% of the total molybdenum; its presence is due to the low pH (2.6) and the molybdenum concentration (ca 0.7mM).

Molybdenum disulfide

The uv spectrum is compared with sodium molybdate in Figure 18 and peaks are given in Table 11.

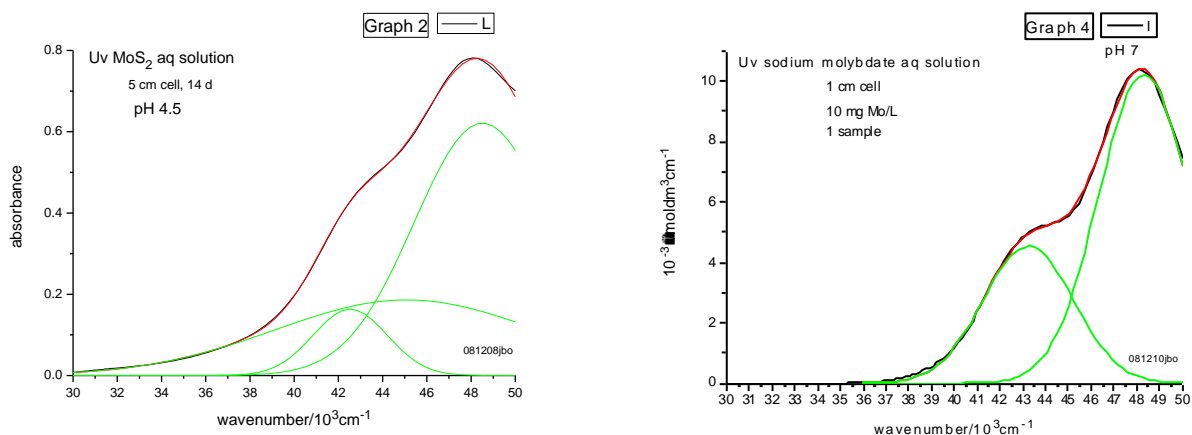


Figure 18. Uv spectra of supernatant water solution from molybdenum disulfide and sodium molybdate. Note that the MoS_2 is for a 5 cm cell path and for sodium molybdate for 1 cm. The MoS_2 intensities are multiplied by a factor of 5.

Comment

The uv spectrum of the MoS_2 supernatant shows the presence of $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$ and $[\text{H}_2\text{MoO}_4]$ with molybdate dominant (see Table 8). The broad background peak is not identified.

Table 11. Uv spectra of molybdenum dioxide and sodium molybdate from the IMO A REACH studies				
	Molybdenum disulfide	REACH sodium molybdate	$[\text{HMoO}_4]^-$	$[\text{H}_2\text{MoO}_4]$
	pH 4.5	pH 7	pH 4	pH <3
Peak I/ 10^3cm^{-1}	48.5	48.3	46.9	46.7
absorbance	0.62			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		10.2	3.5	5.6
Peak II/ 10^3cm^{-1}	42.5	43.2	41.3	42.2
Absorbance	0.16			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$		4.5	1.1	3.6
Peak III/ 10^3cm^{-1}	45.0			
Absorbance	0.18			
$\epsilon/10^3\text{molModm}^3\text{cm}^{-1}$				

Conclusion

The uv spectrum of the water phase from molybdenum disulfide in contact with water shows that the major species are $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$ and $[\text{H}_2\text{MoO}_4]$. They are formed by dissolution of a surface layer of MoO_3 at pH 4.5. Another species remains to be identified.

Conclusions

The uv spectral analysis has enabled us to describe the speciation in water solutions of soluble molybdates (sodium and ammonium molybdates) and in supernatant solutions of suspensions of poorly soluble molybdenum substances (calcium molybdate, molybdenum metal, ferromolybdenum, molybdenum dioxide, molybdenum trioxide, roasted molybdenum concentrate and molybdenum disulfide). The solutions and supernatant liquids contain the molybdate ion and, in addition at lower pHs, protonated molybdate. At biological concentrations and pH the only molybdenum species produced from the molybdenum substances studied is the molybdate, $[\text{MoO}_4]^{2-}$, ion. Read across from sodium molybdate is therefore justified.

The uv analysis provides the following results for each substance.

- ◆ Sodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$. In solution at concentrations 1–10 mgMo/L and pH 7 the molybdate ion, $[\text{MoO}_4]^{2-}$, is the only molybdenum species.
- ◆ Ammonium dimolybdate, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$. The molybdate species in solutions of ammonium dimolybdate is the $[\text{MoO}_4]^{2-}$ ion. There was some protonation of the molybdate ion as expected at pH 5.
- ◆ Ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. The molybdate species in solutions of ammonium heptamolybdate is the $[\text{MoO}_4]^{2-}$ ion. There was some protonation of the molybdate ion as expected at pH 5.
- ◆ Ammonium octamolybdate, $(\text{NH}_4)_4\text{Mo}_8\text{O}_{26} \cdot 5\text{H}_2\text{O}$. The molybdate species in solutions of ammonium octamolybdate are $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$, and $[\text{H}_2\text{MoO}_4]$ consistent with pH 3.3
- ◆ Calcium molybdate CaMoO_4 . The molybdate species in solutions of calcium molybdate are $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$, and $[\text{H}_2\text{MoO}_4]$ consistent with pH 4.
- ◆ Molybdenum metal powder. Molybdenum metal powder suspended in water for 24 h produces a water phase (supernatant) containing only the $[\text{MoO}_4]^{2-}$ ion. Molybdate is formed by dissolution of a surface layer of MoO_3 . There is no evidence of other molybdenum species.
- ◆ Ferromolybdenum. Ferromolybdenum suspended in water produces a water phase (supernatant) containing only the $[\text{MoO}_4]^{2-}$ ion. Molybdate is formed by dissolution of a surface layer of MoO_3 . There is a background of ca 10% which may be due to iron.
- ◆ Molybdenum dioxide, MoO_2 . Molybdenum dioxide suspended in water produces a water phase (supernatant) containing the $[\text{HMoO}_4]^-$ and $[\text{H}_2\text{MoO}_4]$ formed by dissolution of a surface layer of MoO_3 at pH 3.6. Lower valent molybdenum species are absent.
- ◆ Molybdenum trioxide, MoO_3 . Molybdenum dioxide suspended in water produces a water phase (supernatant) containing $[\text{H}_2\text{MoO}_4]$ and $[\text{Mo}_7\text{O}_{24}]^{6-}$. The heptamolybdate represents less than 10% of the total molybdenum; its presence is due to the low pH (2.2) and the molybdenum concentration (ca 0.6mM).
- ◆ Roasted molybdenum concentrate. The supernatant solution from roasted molybdenum concentrate suspended in water has a uv spectrum similar to the spectrum of MoO_3 showing evidence for $[\text{H}_2\text{MoO}_4]$ and $[\text{Mo}_7\text{O}_{24}]^{6-}$. The heptamolybdate represents ca 20% of the total molybdenum; its presence is due to the low pH (2.6) and the molybdenum concentration (ca 0.7mM).
- ◆ Molybdenum disulfide. Molybdenum disulfide suspended in water produces a water phase (supernatant) containing $[\text{MoO}_4]^{2-}$, $[\text{HMoO}_4]^-$ and $[\text{H}_2\text{MoO}_4]$. They are formed by dissolution of a surface layer of MoO_3 at pH 4.5.

Iron(III) molybdate uv spectra – further analysis of the spectra – speciation of molybdenum and iron

Philip Mitchell

20 October 2010

The ultraviolet (UV) spectra of aqueous solutions prepared by extracting iron(III) molybdate with water for time periods have been measured and reported by the Fraunhofer Institute for Molecular Biology and Applied Ecology (IME) commissioned by IMO A (Dr. Thorsten Klawonn: Recording of UV-spectra of aqueous samples from water solubility test. September 16, 2010). I have further analysed their spectra by decomposition into Gaussian peaks. I have included iron(III) in the analysis and incorporated analytical data on the compositions of the solutions previously reported by Fraunhofer.

My Gaussian-analysed spectra are shown in Figure 1(p. 4). The spectra have been re-plotted from the Excel files provided by Fraunhofer using the Origin software: black traces are the reported experimental spectra; green traces are the Gaussian peaks; the red trace is the reconstructed spectrum from the Gaussian peaks. The spectra are plotted on an energy scale (10^3 cm^{-1}) as required for the Gaussian analysis. Details of the measurement are included with each plot. An example of the analysis is given for the 24h extract in Table 1. The fit is excellent ($R^2 = 1$).

Table 1 Gaussian analysis of 24h aqueous extract of iron(III) molybdate

quantity	value	± uncertainty	± % uncertainty	assignment
xc1	48.4	0.00756	0.02	$[\text{MoO}_4]^{2-}$
w1	4.6	0.03383	0.73	
A1	2.2	0.04889	2.24	
xc2	43.0	0.02953	0.07	$[\text{MoO}_4]^{2-}$
w2	3.9	0.06139	1.56	
A2	0.6	0.03235	5.08	
xc3	41.9	0.76834	1.83	Fe^{3+}aq
w3	10.9	0.54299	4.98	
A3	0.6	0.08703	14.27	

xc, peak centre and peak number; w, half width; A, area.

The peak at $48\,000 \text{ cm}^{-1}$ (208 nm) and the shoulder at $43\,000 \text{ cm}^{-1}$ (233 cm^{-1}) are assigned to the molybdate ion as before. The uv spectra of iron(III) species are in the literature (p.4). The iron(III) spectrum is under the molybdate spectrum; the peak positions depend on the species which in turn depends on the pH. For $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (pH < 1) we have a peak at $41\,700 \text{ cm}^{-1}$ (240 nm) and for $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ (pH > 1) peaks at $48\,800$ and $33\,700 \text{ cm}^{-1}$ (205 and 297 nm). With increase of pH as the number of hydroxo species increases the spectrum appears as a broad absorption through the uv region. The pH of the iron(III) molybdate solutions was ca 4.3 (Fraunhofer report) so we expect iron(III) to contribute a rather broad absorption below the molybdate spectra as observed. (The

iron(III) uv intensity is less than the molybdate uv intensity because the iron(III) concentration is lower – see later.)

How the spectra change with time and concentration is shown in Figure2 (time) and Figure 3 (concentration).

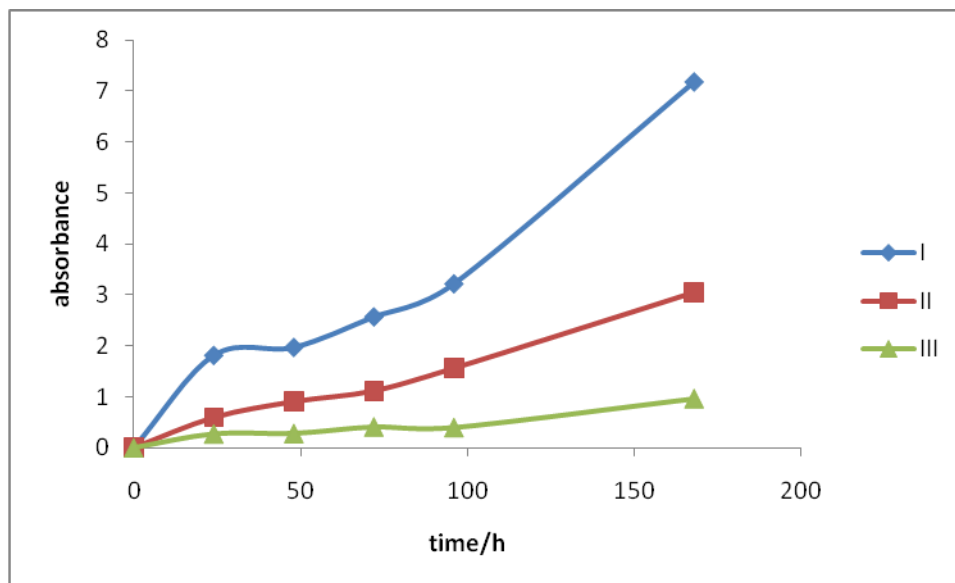


Figure 2. Iron(III) molybdate extracted with water - uv absorbance of molybdate (peaks I and II) and iron(III) (peak III) vs extraction time .

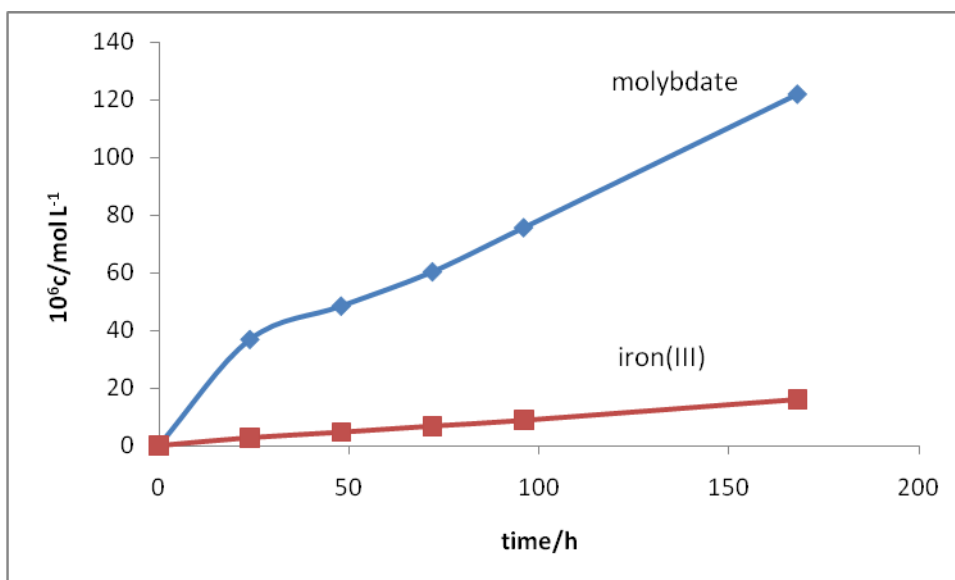


Figure 3. Iron(III) molybdate extracted with water - concentration of molybdate and iron(III) vs extraction time .

From the concentrations and the uv absorbances at selected times we can construct Beer's law plots (absorbance vs concentration) and from the gradients calculate the molar extinction coefficients: Figures 4 and 5.

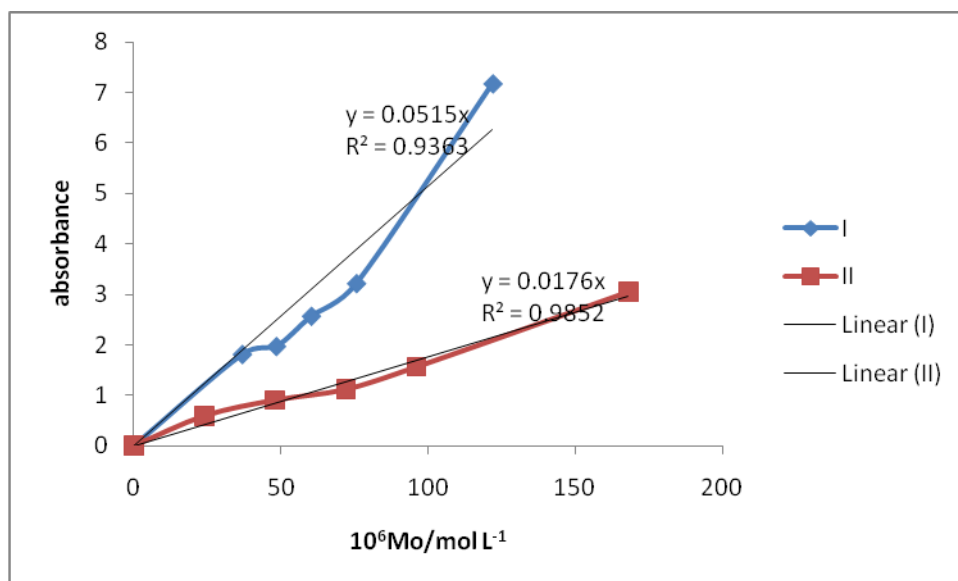


Figure 4. Beer's Law plot for iron(III) molybdate, molybdate peaks I and II.

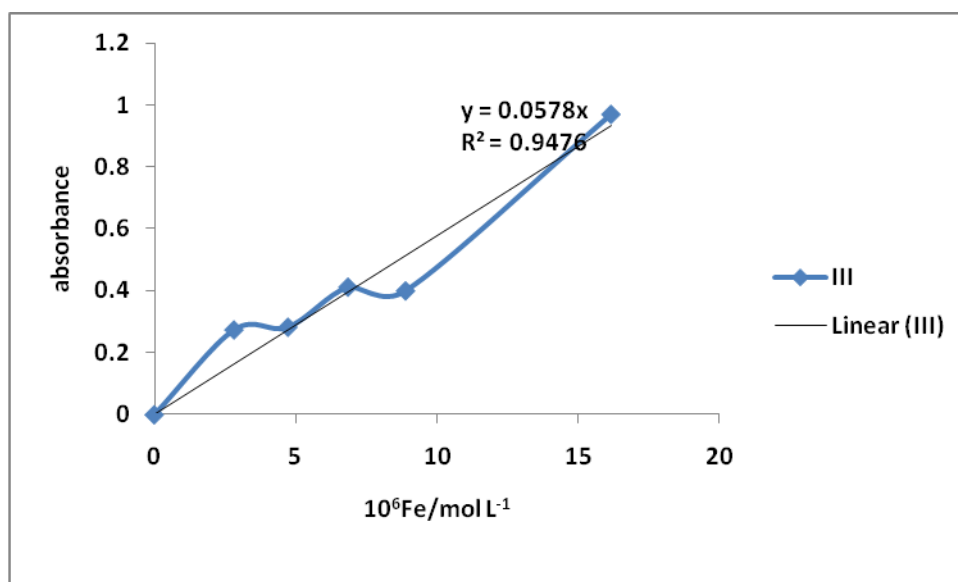


Figure 5. Beer's Law plot for iron(III) molybdate, iron(III) peak III.

The gradients of the Beer's Law plots, the calculated extinction coefficients and the literature values are collected in Table 2. The values are consistent with the presence in the solution of molybdate and iron(III). Our value for the extinction coefficient of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is greater than previously reported values.

Table 2. Extinction coefficients from Beer's Law plots

species and peak	gradient	extinction coefficient/ $\text{mol}^{-1} \text{L cm}^{-1}$	
		this work	previous or literature values
molybdate, I	0.0515	10300	10200
molybdate, II	0.0176	3520	4510
iron(III), III	0.0578	11560	4500

References

P.C.H. Mitchell. Speciation of molybdenum compounds in water. Report for the International Molybdenum Association and REACH Molybdenum Consortium: Ultraviolet spectra and REACH read across. March 2009.

L.N. Mulay and P.W. Selwood, *J. Amer. Chem. Soc.*, 1955, 77, 2693. Hydrolysis of Fe^{3+} : Magnetic and spectrophotometric studies on ferric perchlorate solutions.

A. Stefansson, K.H. Lemke and T.M. Seward, In Proceedings of ICPWS XV (15th Internat. Conf. on the Properties of Water and Steam), Berlin, Sept. 2008, geo 01-09. Iron(III) complexation in hydrothermal solutions – an experimental and theoretical study.

Figure 1. Uv spectra of iron(III) molybdate water extracts. Black trace, experimental spectrum; green trace, gaussian decomposed spectra; red trace, reconstructed spectrum from gaussians.

