

KJ2051-Laboratory course

Spectrophotometric determination of Cr and Mn

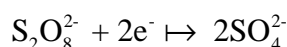
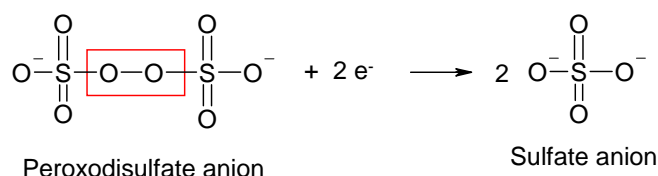
In many samples, Cr and Mn occur as cations (Cr^{3+} and Mn^{2+} , respectively) and cannot be determined by absorption spectrometry because they are not able to absorb light to a large enough extent in this form.

That is why these ions should be first converted to light-absorbing forms ($\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- , respectively) by suitable chemical reactions.

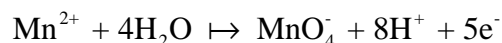
1. Chemical reactions

1.1. Mn^{2+} oxidation by peroxodisulfate

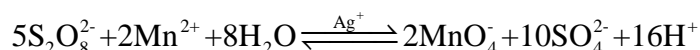
During a redox reaction, peroxodisulfate anion accepts 2 electrons at the central $-\text{O}-\text{O}-$ bond and splits out yielding two sulfate anions:



Mn^{2+} oxidation occurs as follows:

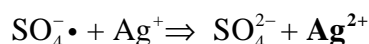


Ag^+ is needed as a catalyst. The *overall* reaction is:

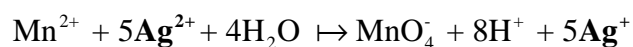


1. 2. Ag^+ catalysis of Mn^{2+} oxidation: mechanism

As a first step, Ag^{2+} ions are first produced by Ag^+ oxidation; peroxodisulfate anion splits into a sulfate anion-radical and a sulfate di-anion:

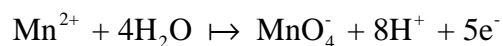


Next, Mn^{2+} is oxidized by a stepwise process involving Ag^{2+} as electron acceptor, according to the following overall reaction:

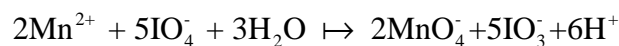


The $\text{Ag}^{2+}/\text{Ag}^+$ system acts as an electron shuttle between manganese and peroxodisulfate.

1.3. Mn²⁺ oxidation by periodate



Overall reaction:



1.4. Cr³⁺ oxidation by peroxodisulfate

In this particular Experiment, samples contain chromium as Cr₂O₇²⁻ and no oxidation is needed. As an exercise, try to write yourself the chemical reaction for Cr³⁺ oxidation by peroxodisulfate.

2. Wavelength selection

Right wavelength selection is a crucial prerequisite in spectrometric analysis.

Wavelength selection is done after an inspection of the absorption spectra for each individual compound. Next rules are applied:

- the absorbance of the compound of interest should be at its maximum;
- no other sample component do absorb light at the selected wavelength.

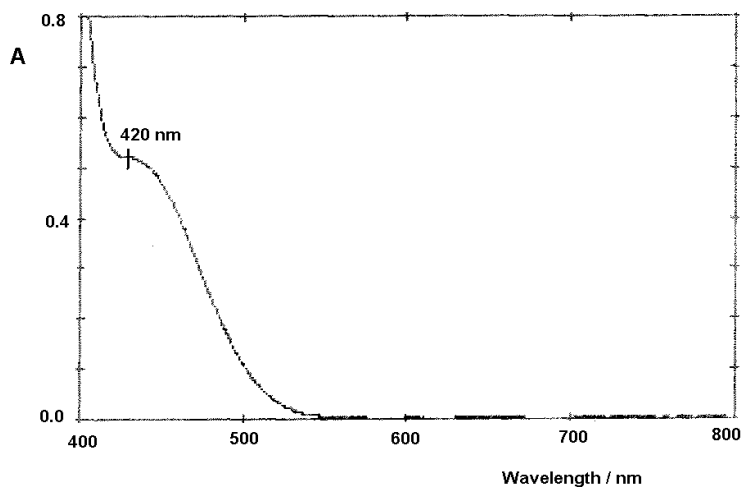


Fig. 1. Absorption spectrum for dichromate ion (Cr₂O₇²⁻).

According to Fig. 1, the dichromate ion spectrum shows a shoulder at 420 nm. This is therefore the selected wavelength for the dichromate ion.

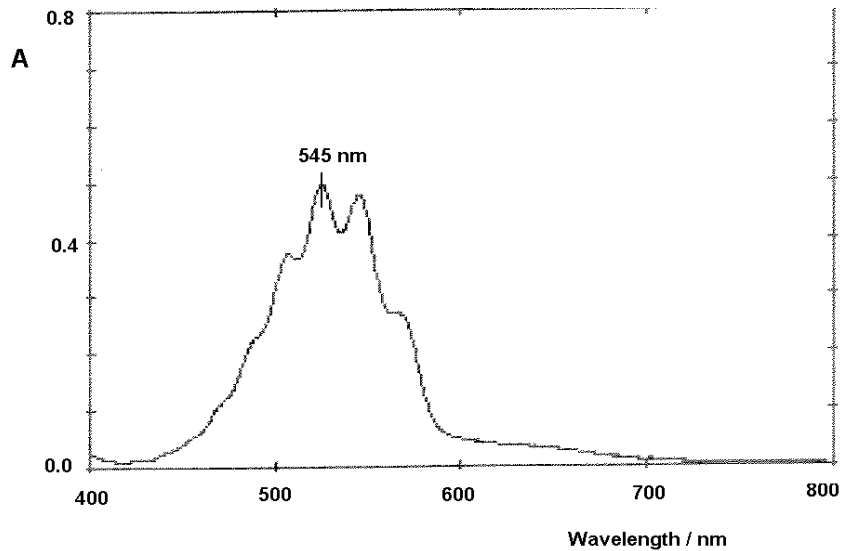


Fig. 2. Absorption spectrum for permanganate ion (MnO_4^-).

According to Fig. 2, the permanganate ion spectrum shows a maximum at 545 nm. This is therefore the selected wavelength for the permanganate ion.

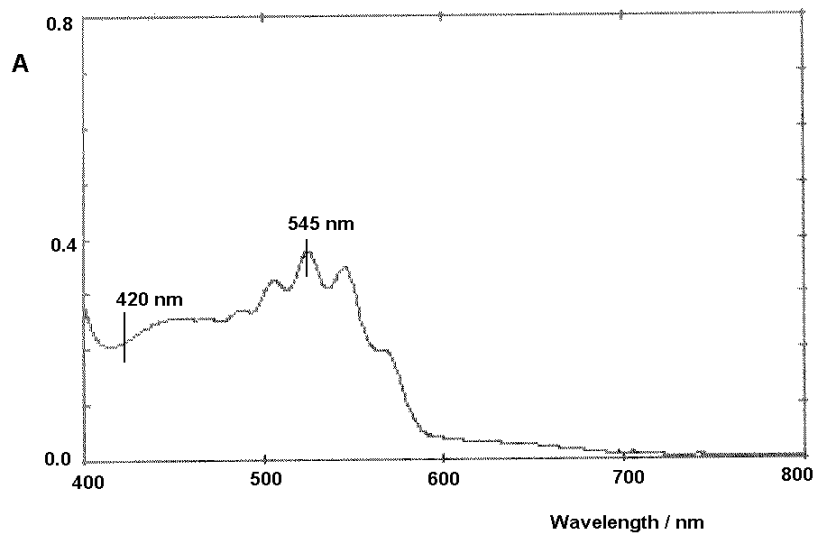


Fig. 3. Absorption spectrum for a solution containing both dichromate and permanganate ion.

If the concentration of these ions is low enough (as it occurs in this Exercise), at each of the selected wavelengths, light is absorbed by only one of the above ions (see Figs. 1 and 2) and no mutual interference occurs. For example, dichromate absorbance at 545 nm is negligible (Fig. 1) and, if permanganate is also present, only this one absorb light at this wavelength. Lambert-Beer law can therefore be applied independently to each ion.

At higher concentrations, mutual interference occurs. In this case, a different approach should be employed in order to determine the concentration of each ion.

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5. Spektrofotometrisk bestemmelse av mangan og krom i blanding

Prinsipp: Konsentrasjonene av mangan og krom i en løsning bestemmes ved å måle absorbansen av Cr(VI) og Mn(VII) ved to forskjellige bølgelengder (440 og 545 nm). Det vises til demonstrasjon av, og bruksanvisning for, spektrofotometeret.

Prosedyre

Bestemmelse av molarabsorbans for mangan og krom

1. Det pipetteres ut 10, 15 og 25 ml av hhv standard 0,002 M MnSO_4 og standard 0,017 M $\text{K}_2\text{Cr}_2\text{O}_7$ i tre erlenmeyerkolber
2. Vann tilsettes til totalt ca 100 ml.
3. Tilsettes (forsiktig) 10 ml konsentrert svovelsyre
4. Tilsettes 2 ml 0,1 M AgNO_3
5. Tilsettes 1 g fast $\text{K}_2\text{S}_2\text{O}_8$ (forsiktig) til hver parallell
6. Rist blandingen forsiktig slik at det faste stoffet løses.
7. Det kokes deretter i ca. 5 minutter
8. Løsningen avkjøles
9. Tilsettes 0,5 g KIO_4
10. Dette kokes i 5 minutter
11. Avkjøl løsningene
12. Overfør disse til 250 ml målekolber. Erlenmeyerkolben og trakten skjules grundig; alt væske samles in i målekolben.
13. Fortynn til merket med vann.
14. Absorbansen måles ved 440 og 545 nm med 0,5 M H_2SO_4 som blindprøve.
15. Molarabsorbansen for mangan og krom ved disse to bølgelengdene beregnes ved å plote absorbans mot konsentrasjon.

Analyse av utlevert prøve

Fortynn den utleverte prøven til 250 ml. Ta ut paralleller på 50 ml med pipette og overfør disse til tre 250 ml erlenmeyerkolber.

Deretter behandles den ukjente prøven som standardløsningene fra punkt 2

Absorbansen måles ved 440 og 545 nm med 0,5 M H_2SO_4 som blindprøve. Konsentrasjonene av krom og mangan beregnes ved hjelp av Beers lov.

Standard 0,002 M MnSO_4 og 0,017 M $\text{K}_2\text{Cr}_2\text{O}_7$ leveres ut.

Oppgaven utføres under detaljert veiledning og det er ingen fast feilgrense.