

Analytical challenges in determining low concentration impurities in high purity manganese sulfate monohydrate

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Manganese is a key element in various lithium-ion battery cathode formulations. This includes lithium nickel manganese cobalt oxide and lithium manganese iron phosphate batteries. Manganese contributes towards structural stability and energy density in cathodes and is typically introduced into precursor cathode active material as manganese sulphate. The presence of impurities in the precursor's raw materials, even in very low concentrations, has a negative effect on the electrochemical performance of cathode materials. The accurate measurement of impurities is therefore crucial to produce high purity manganese sulphate of the required specification. This paper details the difficulties associated with low impurity concentration analysis in a high manganese concentration matrix. The use of various analytical procedures such as ICP-OES, flame atomic absorption spectroscopy, and titration are discussed, as well as the methods developed to overcome manganese interference experienced during these procedures.

INTRODUCTION

South Africa is home to an estimated 70% of the world's manganese resources (US Geological Survey, 2024) and is responsible for approximately half of all manganese exports globally (International Manganese Institute, 2024). Significant portions of South African ore are considered high grade (> 42 % Mn) but have a considerable presence of Mg, Si, Ca, and Fe alongside several other prominent heavy metals.

Mn has found increased use in lithium nickel manganese cobalt oxide (NMC) and lithium manganese iron phosphate (LMFP) batteries. In LMFP batteries, the presence of Mn increases energy density (Hong *et al.*, 2014). In NCM batteries, Mn serves to improve the thermal and structural stability of the cathode (Ko *et al.*, 2023) and maintain battery performance over cycles (Yu *et al.*, 2023). Mn typically joins the NCM battery supply chain in precursor cathode active material (pCAM) as solution made up of dissolved high purity manganese sulphate monohydrate (HPMSM) crystals.

Impurities, even in trace amounts, can have significant downstream effects on the cathode material. This includes influencing the morphology of the cathode material (Yu *et al.*, 2023) such that electrochemical properties, lifetime, and stability are altered (Nasser and Petranikova, 2021). Stringent specifications are therefore required by consumers of battery grade HPMSM, with typical specifications of alkali earth metals < 50 mg kg⁻¹ and heavy metals between 1 and 10 mg kg⁻¹. Battery formulations are, however, a developing story with impurity specifications, dopant, and coatings that change frequently. Accurate and reproducible impurity analysis is therefore an imperative for HPMSM manufacturers to respond to the evolving needs of customers.

ANALYSIS OF HPMSM

General

HPMSM crystals require dissolution with ultra-pure water for most analytical methods. The amount of water added is a trade-off between diluting analytes below limits of detection or operating with a solution of elevated total dissolved solids (TDS) brought about by the abundance of Mn. The high TDS and viscosity of samples can lead to significant analytical challenges. This includes an increased risk of blockages in tubes and the nebuliser, as well as physical interference during analysis. Therefore, frequent cleaning and inspection of equipment forms a vital part of the analytical procedures. Surfactants added to samples, like Triton X-100, also play an important role in preventing blockages.

Removal of all or some of the Mn in the sample matrix could be achieved using ion exchange resins or the precipitation of an insoluble Mn compound. In practice, however, these complications are avoided as they can produce both losses or gains in measured trace impurities.

Flame atomic absorption spectroscopy

Flame atomic absorption spectroscopy (FAAS) is ideal for the rapid analysis of individual elemental impurities. FAAS analysis of impurities does, however, have some challenges. Ca is problematic to analyse, as the high sulphate concentration of HPMSM results in the formation of CaSO_4 . This salt is difficult to volatilise in the FAAS flame and results in a suppressed reading (Skoog *et al.*, 2007). Suppression can be overcome with elevated flame temperatures, or more conveniently with the addition of 2.7 g L^{-1} LaCl_3 . This reagent is dosed as it preferentially reacts with sulphates and promotes the formation of the highly volatile CaCl_2 (Kántor, 1987). Ionisation in high temperature FAAS flames can also be problematic, as the absorbance behaviour of ionised elements differs from that of unionised elements (Sanui and Pace, 1968). KCl is therefore added (2 g L^{-1}) as an ionisation buffer that shifts the ionisation equilibrium of the analyte.

Inductively coupled plasma optical emission spectrometry

While FAAS is more cost-effective, the higher precision and ability to analyse multiple elements simultaneously make inductively coupled plasma optical emission spectrometry (ICP-OES) preferable. Wavelength selection is done to maximise the detected intensity and signal to background noise ratio while avoiding spectral interference from other elements. The wavelengths found to work best for HPMSM detection are presented in Table I.

Table I. Preferred elemental wavelengths used for radially configured ICP-OES analysis of HPMSM

Element	I/II*	Wavelength, nm
Al	I	396.152
B	I	249.677
Ca	I	422.673
Cd	II	226.502
Co	II	228.616
Cr	II	284.325
Cu	II	224.700
Fe	I	373.486
K	I	766.491
Mg	II	279.553
Na	I	589.592
Ni	I	341.476
Sc	I	335.373
Sc	II	361.384
Sc	II	256.023
Si	I	251.612
Zn	I	213.856

* I = atomic wavelength, II = ionic wavelength

The wavelengths selected during method development should always be checked for interferences. This can be done by selecting additional wavelengths for comparison.

The effects of the sample matrix can be accommodated with matrix matching, where the blank and calibration standards are dosed with ultra-pure manganese sulphate at similar concentrations to those of the samples. However, the cost of manganese sulphate standards with low enough impurities for this method is prohibitively high. The standard additions technique can also be used to accommodate matrix effects and is discussed in the next section. It is, however, impractically time-consuming when used for each sample.

An internal standard is recommended as a convenient and cost-effective method to correct for physical interference and matrix differences between calibration standards and samples (Higson, 2003). The internal standard is added at an equal known concentration to blanks, samples, and calibration standards. Most ICP-OES instruments are capable of internally adjusting sample concentration readings based on variations between the internal standard signal in calibration standards and samples.

Sc at a concentration of 1 mg L⁻¹ has been found to be a suitable internal standard due to the low probability of Sc occurring in the sample and the availability of strong, interference-free wavelengths for analyses. Table I shows three different Sc wavelengths used as internal standards in HPMSM analysis. General practise is to only reference ionic standard wavelengths with ionic sample wavelengths while referencing atomic standard wavelengths with atomic sample wavelengths (Ivaldi and Tyson, 1996). Additionally, a Sc wavelength similar to the analyte wavelength should ideally be chosen.

The high Mn concentration makes the development of ICP-OES methods for the simultaneous determination of Mn and impurities challenging. As with matrix matching, ultra-high purity Mn standards are required to ensure no further impurities are introduced when making up calibration standards. Additionally, high concentrations of analyte may result in the self-absorption of emitted

spectra (Chausseau *et al.*, 2001). The phenomenon is illustrated in Figure 1, where some photons emitted by Mn at 279.482 nm are reabsorbed by Mn ions in cooler parts of the plasma. This leads to an apparent inversion of the intensity peak that will report suppressed concentrations. While ICP-OES methods can be optimised for Mn analysis, potentiometric determination has been found to give more reproducible results at greater cost effectiveness.

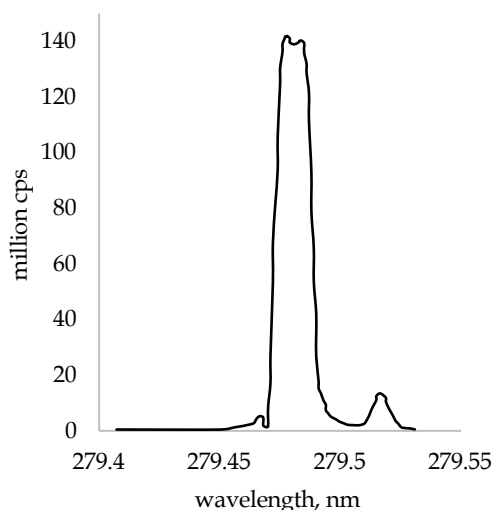


Figure 1. Self-absorption observed in Mn 279.482 nm wavelength of HPMSM analysed by ICP-OES.

Radial or axial plasma observation can be used for HPMSM analysis. The axial configuration tends to result in lower limits of detection when compared to radial configuration, although the standard error tends to be greater for some elements. This is shown in Figure 2, where the method detection limit (MDL) and standard error of radial and axial configurations were determined from calibration standards prepared for HPMSM analysis. Axial configuration is, however, significantly more prone to interference from matrix effects (Chausseau *et al.*, 2001) and is typically only recommended when matrix matching is available (Bois *et al.*, 2016).

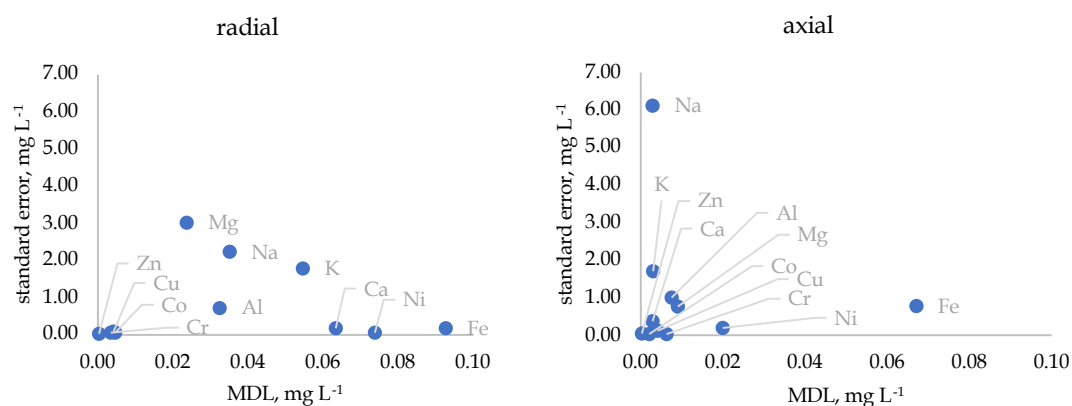


Figure 2. Comparison of MDL and standard error for radial and axial ICP-OES configuration.

Finally, use of high purity Ar gas is also essential for ICP-OES analysis as gas impurities have been found to interfere with spectra in HPMSM analysis.

Inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is widely regarded as a more accurate analytical method than both ICP-OES and FAAS (Wilschefski and Baxter, 2019) with significantly better

precision and lower limits of detection (Baralkiewicz *et al.*, 2007). As with ICP-OES, Sc has been found to be a suitable internal standard to account for some matrix effects.

However, interference is also prevalent in ICP-MS when analysing impurities in manganese sulphate solution. The high concentration of sulphates in the matrix lead to the formation of multiple polyatomic sulphur-oxygen molecules with the same mass to charge ratio as analytes (Taylor, 2001). Similarly, the most abundant isotope of argon ions from the plasma have the same mass to charge ratio as the most abundant isotope of calcium (May and Wiedmeyer, 1998). This is a source of significant interference when trying to determine Ca concentration.

Manganese titration

HPMSM crystals should theoretically have a Mn concentration of 32.51%. Calculating the purity of HPMSM by relating the measured Mn concentration to the theoretical concentration does not yield meaningful results as the effect of trace impurities on Mn concentration is too small to be determined precisely. A Mn concentration specification is still, however, typically requested from customers as a quality assurance measure.

Mn can be accurately measured in dissolved HPMSM by potentiometric titration, where Mn^{2+} is oxidised by 0.15 N potassium permanganate in the presence of excess pyrophosphoric acid as follows (Lingane and Karplus, 1946):



Fluoride ion selective electrode

Fluoride can be determined with an MDL $< 1 \text{ mg kg}^{-1}$ using a fluoride ion selective electrode (ISE). The electrode is, however, sensitive to pH as the electrode is prone to interference from H^+ and OH^- ions (Skoog *et al.*, 2007). The suitable pH range for sample analysis is between 5 and 8. Additionally, total ionic strength buffer III (TISAB III) should be added to samples to improve accuracy by increasing the ionic strength and suppressing interfering ions.

Fluoride ISEs are prone to memory effects and require conditioning for low concentration measurements. This typically involves keeping the electrode in ultra-pure water for around 30 minutes before analysing a sample. The adequacy of the conditioning procedure should be confirmed by the analysis of standards.

Other analytical techniques

Colorimetric techniques for low concentration impurity detection in manganese sulphate solution were reported by Jacobs *et al.*, (1946), but these have been found to have significant pH sensitivity and have been unable to produce consistent results.

The MDL for X-ray diffraction (XRD) analysis typically sits at around 1% by mass and is too poor for the determination of elemental impurities in HPMSM. XRD might be convenient for the confirmation of the correct water of crystallisation in HPMSM (i.e., monohydrate rather than tetrahydrate), although a Karl Fischer titration or gravimetric analysis would be more precise.

VERIFICATION OF ANALYTICAL RESULTS

The meaningfulness of HPMSM impurity analyses hinge on whether the analytical results reported are representative of the true concentration. Various approaches can be taken to provide confidence, such as the use of standard additions, method limit calculations, statistical process control, mass balances, and tests for robustness. The regular comparison of sample analyses with different instruments and at external laboratories is also a key part of result verification.

Standard additions

Conventional calibration standards made up from a composition of known analyte concentrations may not fully represent all the species found in samples. The effects of the sample matrix on analytical results can, however, be assessed with the standard additions technique. If the concentration of an analyte is

sequentially increased by known amounts, a linear relationship between concentration and the responding analytical instrument signal may be determined. The concentration of analyte in the original sample can then be inferred from the relationship as it corresponds to the intercept of the concentration axis (Higson, 2003).

The standard additions technique is illustrated as an example in Figure 3 for the determination of the Fe concentration in an HPMSM sample. In Figure 3a), it can be seen that Fe added to the sample results in a linear increase in the absorbance detected by the FAAS instrument. If this relationship had to be replotted to intercept the origin (Figure 3b), the x-axis would correspond to the actual Fe concentration. This new absorbance-concentration relationship can then be used to infer the actual Fe concentration from the measured absorbance of the original sample.

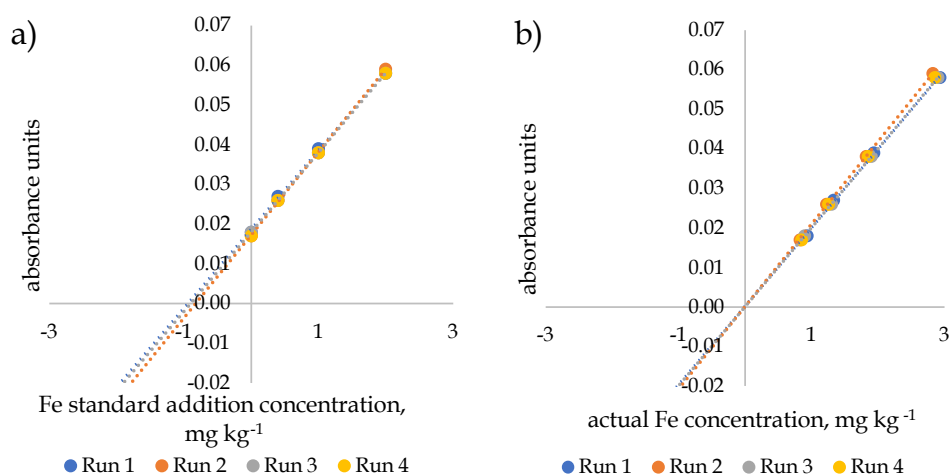


Figure 3. Standard additions method applied to HPMSM for determination of Fe concentration by FAAS.

Method limits

Analyte concentrations reported within the range of prepared calibration standards are the most trustworthy analytical results. However, the low concentrations of impurities in HPMSM often approach the lower analytical limitations of instruments used. The reliability of reported low analyte concentrations should therefore be determined. This can be done by assessing where the concentration lies in relation to the MDL and method quantitation limit (MQL).

The MDL is the lowest concentration in an analytical method at which the instrument can reliably distinguish the analyte from the blank. Concentrations measured below the MDL should be considered as undetected. The MQL, on the other hand, is the lowest concentration at which the method can report results with satisfactory precision (Armbruster and Pry, 2008). Concentrations between the MDL and MQL should be considered as qualitative indicators of the presence of an analyte, and concentrations greater than the MQL can be quantitatively interpreted. Typically, the MDL and MQL are chosen to lie at 3 and 10 standard deviations of the measured analyte signal respectively (MacDougall *et al.*, 1980). As an example, these limits in ICP-OES analysis can be calculated during each calibration as:

$$\text{MDL} = \frac{C_1 - C_0}{I_1 - I_0} 3\sigma \quad [2]$$

$$\text{MQL} = \frac{C_1 - C_0}{I_1 - I_0} 10\sigma \quad [3]$$

Where C_1 and C_0 are the concentrations in mg L^{-1} of the maximum calibration standard and blank respectively, and I_1 and I_0 are the raw intensities in cps of the maximum calibration standard and blank respectively. σ is the standard deviation of the blank intensity in cps.

Statistical process control

The use of an internal quality control sample is also recommended so that a statistical control approach can be taken. If the same HPMSM sample is analysed each time an instrument is calibrated, the concentration of analytes can be recorded as a function of time. This allows for the monitoring of the analytical procedure stability (Mullins, 1994). Furthermore, limits can be calculated to warn of instrumental drift or alert when analysis is no longer statistically in control. The warning limit (WL) and action limit (AL) for analytes can be calculated as (Harvey, 2011):

$$\text{WL}_i = \bar{C}_i \pm 2\sigma_i \quad [4]$$

$$\text{AL}_i = \bar{C}_i \pm 3\sigma_i \quad [5]$$

Where \bar{C}_i and σ_i are the respective mean and standard deviation of concentrations for all the quality control sample measurements of a particular analyte.

Mass balance

Mass balances are an important part of analytical method verification. The total mass of each analyte fed into the crystalliser should be equivalent to the sum of the mass of each analyte reporting to the crystals and mother liquor. Errors in the mass balance could be indicative of mechanical losses, contamination, or analytical inaccuracies.

Method robustness

Finally, the robustness of a method can be tested. This is done to investigate sources of variability within an analytical method (Vander Heyden *et al.*, 2001) and may be used as an indicator of method's reproducibility (Ferreira *et al.*, 2017). Ruggedness tests can be carried out by evaluating the effects of small changes made to the analytical procedure on reported impurity concentrations. A two-level factorial design of variables such as the mass of sample analysed, sample dilution, pH, and reagent concentration is recommended.

CONCLUSIONS

The accurate measurement of impurities in HPMSM is crucial for the production crystals that meet required customer specifications and allow for agreement between buyer and seller. Analysis with ICP-OES and FAAS require method development with considerations for matrix effects alongside physical, chemical, and spectral interferences. Additionally, the reporting of analytical results should only be interpreted meaningfully if they are verified by a variety of strategies.

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