

APPLICATION NOTE

T2O-AN-306

MANGANESE METHOD

The following application note explains the procedure for the detection of Manganese using the HM3000 Metalyser®.

PLEASE READ THIS APPLICATION NOTE CAREFULLY. TRACE2O® HAS ALTERED THE NAMES OF SOME REAGENTS FOR SIMPLICITY AND SO THE PROCEDURE MAY BE DIFFERENT FROM THAT FOLLOWED PREVIOUSLY.

Equipment:

- **HM3000 Kit**
- **HM4 Buffer** (Previously M6 Buffer A solution)
- **HM5 Buffer** (Previously M6 Buffer B solution)
- **MN40 Mn Standard** (Previously M6 Standard (4ppm))
- **HG100 Thick Hg Plating Solution** (Previously M6 Conditioning Solution)

Electrode conditioning:

- Polish WE1 Electrode to a mirror finish and check using a magnifier that no scratches or scuffs are present.
- Half-fill the sample analysis beaker (SAB) with **HG100 Thick Hg Plating Solution** and fit to the Sonde.
- Select 'M6 Conditioning' from the 'Measurements available menu' then click 'Condition Electrode' on the Analysis panel.
- The M6 conditioning step will take approximately 10 minutes.
- Once completed, return the **HG100 Thick Hg Plating Solution** to the **HG100 Thick Hg Plating Solution** bottle and rinse the Sonde and SAB with the Electrode Rinse Solution and/or deionised water.

Sample preparation:

- Using a plastic syringe, add **14ml HM4 Buffer** to the SAB.
- Add 56ml of sample water to the SAB
- Using the pipette, add **280µl HM5 Buffer** to the SAB.

There are three methods for carrying out the analysis. The single-point standard addition is the fastest option, using two data points to calculate concentration. This is also less accurate. The multi-point standard addition uses four data points to calculate concentration, and allows repeat scans for stabilisation purposes. This method takes longer and uses more chemicals. The calibration option is designed for rapid analysis of several samples with a similar matrix (i.e. several samples from different points along the same river bank).

Analysis (single-point standard addition method)

- Fit the SAB to the Sonde.
- Select 'Mn' from the 'Measurements Available' drop down menu, then click 'Condition Electrode' from the analysis panel and wait approximately two minutes for it to complete.
- Click 'Standard Addition' in the analysis panel. Wait approximately two minutes until prompted to add 20ppb of the standard. When prompted use the pipette to add 280µL of the **MN40 Mn Standard** into the SAB and click 'OK'. The analysis will continue to run for approximately two further minutes, then the results will be displayed.

Result (single-point standard addition method)

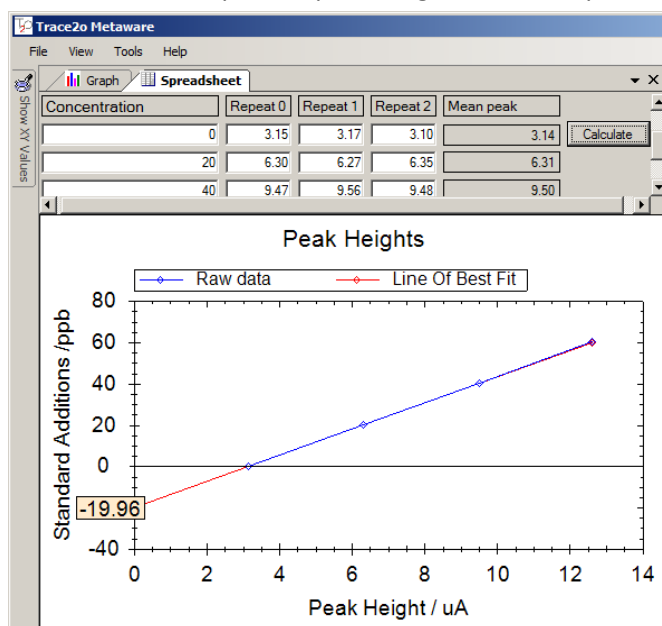
- The result(s) are shown in the Analysis window until 'Ok' is clicked. Following this the results are displayed as a graph on the graph tab and the ppb results will be automatically entered into the results log. There will two graphs displayed, the first is the scan of the original sample concentration and the second is after the standard addition. If Mn has been detected the peak identified as Mn will be marked up as such and the original sample concentration reported in ppb.

Analysis (multi-point standard addition method)

- Fit the SAB to the Sonde (If not using submersion method).
- Select 'Mn' from the 'Measurements Available' drop down menu, then click 'Condition Electrode' from the analysis panel and wait approximately two minutes for it to complete.
- On the Control panel, ensure that Deposition Time is set to 60 seconds. Ensure that 'Background subtraction' is checked.
- Run the stirrer as required to dissolve the buffer into the sample water.
- Click 'Start Analysis' and wait for approximately 1 minute for the graph to be displayed. Repeat until stable. Note that the reading displayed in ppb should be ignored for this method.
- Using the micropipettes, perform a standard addition from the **MN40 Mn Standard** bottle. Use an appropriate addition volume for the sample volume and desired concentration. For better accuracy, a standard addition should be as close as possible to the expected sample concentration. For example, if 10ppb Mn is expected in the sample, the standard addition should add a further 10ppb.
- Reminder – to calculate addition volume, use the following formula:
Standard addition vol. (mL) = $\frac{\text{Sample vol. (mL)}}{\text{Standard conc. (ppb)}} \times \text{Addition conc. (ppb)}$
For example, with a sample volume of 56mL, standard concentration of 4ppm (or 4000ppb) and a desired addition concentration of 10ppb, the standard addition volume would be:
 $\frac{56}{4000} \times 10 = 0.14\text{mL} = 140\mu\text{L}$
- Click 'Start Analysis' and wait for approximately 2 minutes for the graph to be displayed. Repeat if required.
- Repeat the standard addition/Start Analysis procedure a further two times.

Result (multi-point standard addition method)

- To calculate the peak height, first position the stylus over the data-point you wish to use as the right hand side of the peak, then tap-and-hold the stylus and click 'calculate peak'. If a valid point is not found this function will be greyed out.
- Move the stylus to the left hand side of the peak and tap once. The baseline will be drawn in and the peak height shown, reported as a current (μA).
- To calculate the concentration, input the peak heights into the spreadsheet tab.



The table has four possible entries for the sample concentration. The first entry would normally be zero, as this is the unknown concentration of the sample that is trying to be established. The second, third, and fourth entries would be the sample concentration after each standard addition. In the above example three standard additions are performed each of 20ppb. The peak heights are calculated for each of the additions and entered in the table. To achieve greater accuracy, repeat analysis can be run after each addition to give an average over three readings although it is not necessary to fill the table. When all the data is entered, click **Calculate**. The mean peak heights will be calculated and a graph of concentration vs peak height plotted. A line of best fit will be drawn through the data and the y-intercept shown, which corresponds to the unknown sample concentration for the metal of interest. The value is shown as a negative because this indicates the amount which needs to be added to each of the data points to make the line of best fit go through the origin which in this case is 19.96ppb.

Analysis (calibration method)

- Fit the SAB to the Sonde.
- Select 'Mn' from the 'Measurements Available' drop down menu, then click 'Condition Electrode' from the analysis panel and wait approximately two minutes for it to complete.
- Click 'Calibration' in the analysis panel. Wait approximately two minutes until prompted to add 20ppb of the standard. When prompted use the pipette to add 280 μL of the standard into the SAB and click 'OK'. The analysis will continue to run for approximately two further

minutes until prompted to add another 20ppb of standard. Repeat the addition process and click 'ok'. The analysis will run for another two minutes before completing the calibration.

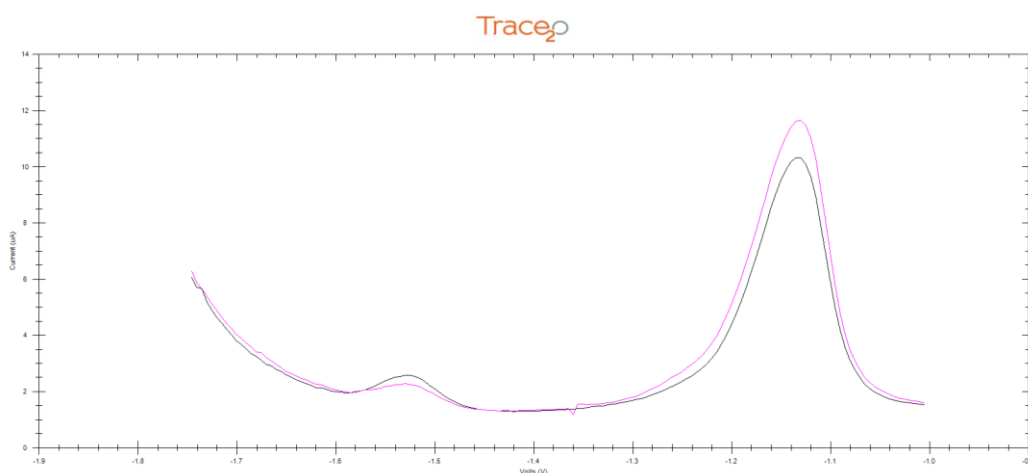
- Once the calibration has been completed several consecutive analyses can be carried out.
- Click 'Analyse Sample' on the analysis panel and wait approximately two minutes for the analysis to complete.

Result (calibration method)

- The result(s) are shown in the Analysis window until 'Ok' is clicked. Following this the result(s) are displayed as a graph on the graph tab. If Mn is present a peak will be seen in the graph which will be marked up as Mn and the calculated sample concentration displayed.

Result

- Manganese appears as a broad peak at around -1.55V. Zinc will appear to the right, at around -1.15V. Disregard the Zinc peak, as this is merely required for co-deposition and does not affect the outcome of the result.



LOD

- The Lower LOD is 5ppb, upper LOD is 200ppb.
- To increase the range the sample can be diluted using Ultra-pure de-ionised water. Other water types could introduce contamination.

Interferences

- Extremely acidic sample water may affect the quality of the analysis.
- Solutions are available for combating interferences in the sample. These may be specific to particular water types or conditions. For further information, please contact Trace2o® Technical Support department – technical@trace2o.com