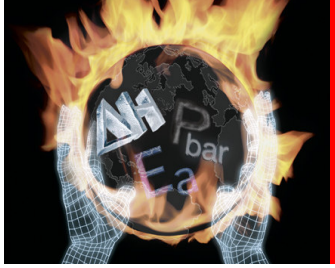
Micro Reaction Calorimeter - µRC™
Technical Application Note 5
End Point Determination of Acid Base Titration



Introduction

Measurement of a known reaction enthalpy is a useful tool to assess the performance of any instrument. Here, a standard calorimetry test is performed using the aqueous reaction of sodium hydroxide and nitric acid according to the following reaction scheme.

$HNO_{3\ (aq)} + NaOH_{\ (aq)} \rightarrow H_2O_{\ (l)} + KNO_{3\ (aq)}$

The standard enthalpy of neutralisation for hydrogen ions by hydroxyl ions for strong acids/bases is –57.3 kJ mol^{-1}.

This experiment will be used to demonstrate that the Micro Reaction Calorimeter (µRC™) from THT can be used to accurately measure the enthalpy of this and similar processes, and that it can determine titration end points.

Experimental

In this experiment the sample vial was made up with 1 mL of a 0.05M sodium hydroxide solution and a standard magnetic stirrer. This vial was then placed in the sample holder in the calorimeter. A 100 µL syringe of 1M nitric acid solution was fitted to the instrument.

The experiment was set up to perform twenty 5 µL injections of the acid into the base and to monitor the heat evolved from this process. It was expected that a full neutralisation of the base should occur after 10 injections (50 µL).

Results

Each injection gives a large peak in the heat signal of the instrument. An increase in heat output corresponds to an exothermic process occurring in the vial.

It is important to note that the first injection in a titration experiment typically gives a smaller heat signal than subsequent injections. It has been suggested that this is caused by the pressure change when piercing the septum pushing some of the sample into the syringe, although the phenomenon has not been fully explained.

The figure below shows the results from the injections overlayed in the analysis software. A table of integrated peaks is also shown to illustrate the reproducibility of the initial peaks and the subsequent end-point of the titration.

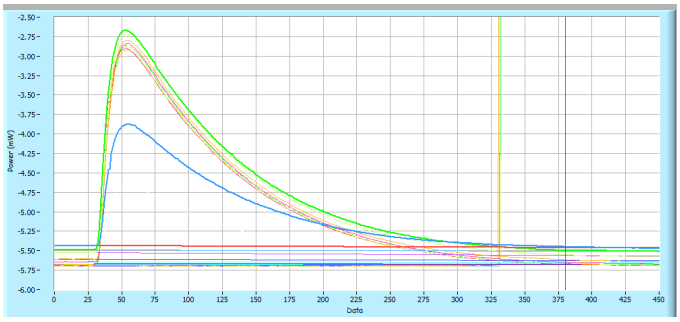


Figure 2: heat signals for 5 µL HNO_3 injections into NaOH

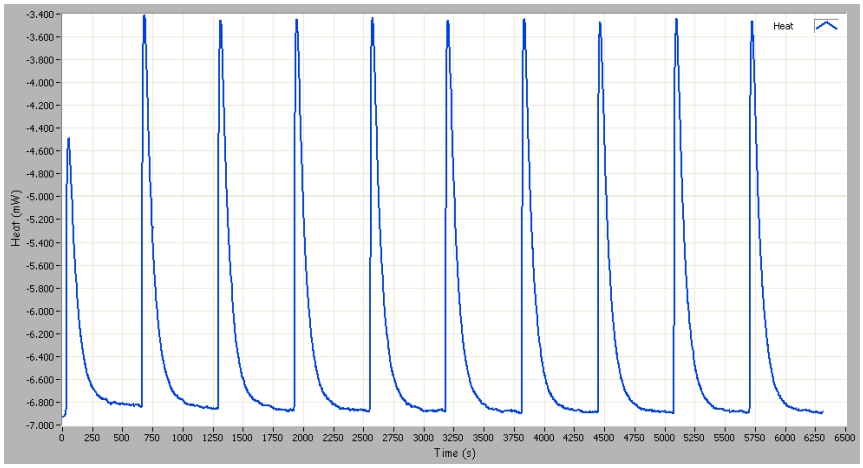


Figure 1: typical heat signal from an acid/base titration

thermal hazard technology

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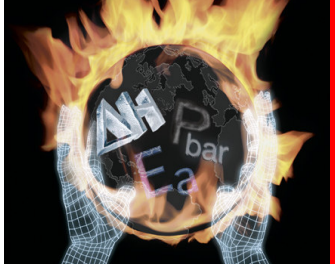

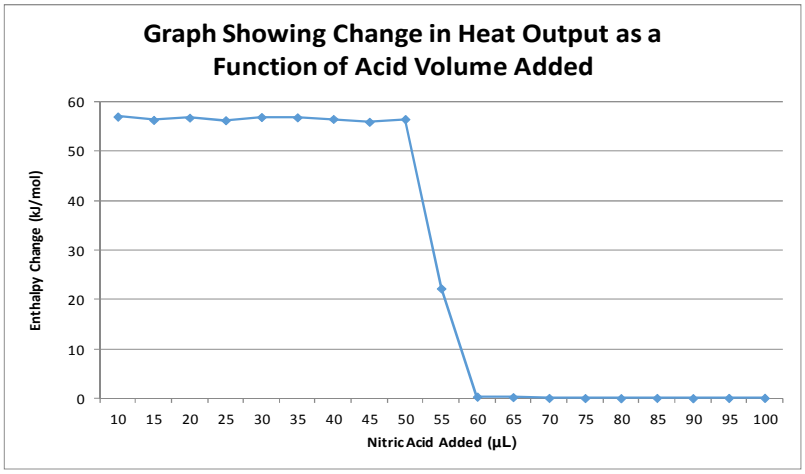

Figure 3: graphical representation of enthalpy changes to illustrate titration end point

Peak	Area (mJ)	Enthalpy (kJ/mol)
1	156.9	31.38
2	284.9	56.98
3	281.6	56.32
4	283.8	56.76
5	281.2	56.24
6	284.4	56.88
7	284.1	56.82
8	282.5	56.50
9	279.7	55.94
10	282.4	56.48
11	111.1	22.22
12	1.5	0.30
13	1.0	0.20
14	0.2	0.04
15	0.1	0.02
16	0.0	0.00
17	0.2	0.04
18	0.0	0.00
19	0.2	0.04
20	0.3	0.06
average (2-10)	**282.4**	**56.55**

Figure 4: heat integrals for 5 µL HNO_3 injections into NaOH

These results suggest the end point occurs at around peak 10, which corresponds to an equimolar solution of acid and base.

The enthalpy of reaction for this process can be seen to be -56.6 kJ mol^{-1}. The small difference between this and the literature value of –57.3 kJ mol^{-1} may be due to the contents of the syringe being slightly cooler than the solution in the vial, although it is within the typical error margin of the instrument (± 2%).

Discussion and Conclusions

These data show the excellent consistency of the µRC™ for collection of reaction enthalpy data. The enthalpy of neutralisation has been determined with good accuracy, and the drop in heat output occurs at the expected titre based on the number of injections.

Figure 5: the µRC from THT