5.4 Enthalpimetric analysis

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Enthalpimetric analysis is the generic designation for a family of analytical methods in which the enthalpy change of a chemical reaction is measured, directly or indirectly, in order to perform a quantitative determination of a reactant or catalyst. Normally at least one reactant is a liquid or solution.

Since $Q_p = (n)(\Delta_r H)$, where $Q_p$ is heat into the reacting system at constant pressure, $n$ is the chemical amount (amount of substance) of analyte, and $\Delta_r H$ is the enthalpy of reaction per amount of analyte, the measurement of $Q_p$ allows calculation of $n$ if $\Delta_r H$ is independently known.

Enthalpimetric analysis or enthalpimetry is a subset of calorimetry in which the system is maintained at constant (usually atmospheric) pressure, and the emphasis is on a quantitative determination in a reasonable length of time. In nearly all cases, at least one reactant is a liquid or solution.

Analytical solution calorimetry is a synonymous designation that may be used but is not preferred. Thermochemical analysis has been used but is not recommended because of potential confusion and overlap with the methods of thermal analysis. The adjective thermometric has also associated with the names of some of these methods, but is not recommended as a general designation. This usage is valid only if temperature is the primary measured quantity, and also, when used by itself (i.e."thermometric analysis") does not necessarily denote the fundamental reliance on the enthalpy change of a chemical reaction.

All instruments that measure heat effects are called calorimeters. The distinction here is in the primary purpose in performing an experiment with that instrument.

Inasmuch as the calorimetric methods of thermal analysis (DTA, DSC) are widely practiced as a means to analyze solids, it is very helpful to have a distinct term to describe calorimetric analysis based upon a chemical reaction involving gaseous, dissolved or suspended analytes.

5.4.2 Individual techniques

Direct Injection Enthalpimetry (DIE)

Direct injection enthalpimetry is an analytical method in which a reactant is injected into a calorimetric vessel containing another reactant. The enthalpy change of the ensuing reaction is measured and directly related to the amount of the limiting reagent (usually the analyte). In some variants used for catalyst assays, the initial rate of heat change is the
measured variable. Modifications for the use of gaseous reagents, suspended solid phases, or catalysts are possible and are of considerable importance.

The equipment for performing DIE may be any of several types of batch injection calorimeters. An isoperibol-type calorimeter is most common where speed in making the measurement is important.

If the experiment determines information other than amounts of analytes, an acceptable synonym is batch injection calorimetry. Other terms which have been used in the literature, but are not recommended, include the concentration thermometric technique and the direct thermometric method.

The plot of temperature vs time or heat change vs. time which is produced in DIE may be referred to as an enthalpogram. The use of the term thermogram is not recommended because it is too general and overlaps with other fields.

**Thermometric Titration**

Thermometric titration is an analytical method in which one reactant (the titrant) is added continuously or stepwise to an adiabatic or isoperibol vessel containing another reactant. The enthalpy change(s) of the ensuing reaction(s) causes temperature changes which, when plotted versus volume of titrant, may be used to find the titration endpoint(s).

This is the preferred term for experiments producing plots of temperature vs. volume of titrant in which the main goal is a quantitative determination. Nonetheless, when a calorimetric vessel is used, such that the heat capacity is known, thermodynamic parameters may also be estimated from such experiments. An acceptable synonym in that case is enthalpimetric titration. The use of the adjective thermometric is justified because of widespread historical and current usage, and because a titration of necessity implies a chemical reaction. The term thermometric enthalphy titration has been used, but is not recommended. Methods in which the titrant is a catalyst for an indicator reaction that occurs after the endpoint for the analyte reaction should be called thermometric titration with catalytic endpoint detection, not catalytic thermometric titration.

The plot of temperature (change) vs. volume of titrant is called a thermometric titration curve, or an enthalpimetric titration curve.

**Calorimetric Titration**

A calorimetric titration is a titration performed in a calorimeter which produces a plot of heat change vs. volume of titrant. This is the preferred term for experiments in which the main goal is the measurement of thermodynamic parameters. Because such experiments may be performed in any of a variety of types of calorimeters with varying degrees of calorimetric accuracy, it is important that the reporting of such results include an
assessment of accuracy and precision. This term stands in contrast to the main emphasis in enthalpimetric analysis.

**Flow Injection Enthalpimetry**

Flow injection enthalpimetry is used to describe several related methods in which a transient temperature change in a flowing liquid stream, caused by a chemical reaction, is used to quantitatively determine an analyte. The analyte is introduced as a discrete liquid sample (i.e. test portion) into the flowing stream.

This definition limits the scope to experiments with primarily an analytical emphasis, performed in a flow injection calorimeter. This maintains a clear distinction from classical flow calorimetric methods where reagents are combined continuously in flowing streams, or where the heat effect is measured via the flowing of a fluid over a reaction vessel.

Flow injection calorimeters vary in the nature of the reaction vessel, with immobilized enzymes sometimes used. These experiments would be appropriately described as "immobilized enzyme flow injection enthalpimetry".

An acceptable synonym is *enthalpimetric flow injection analysis*. Other non-recommended terms which have been used in the literature include *peak enthalpimetry*, and *enzyme thermistor*. *Flow enthalpimetry* has been used to describe the flow injection technique, but its use for this purpose is discouraged.

**Continuous Flow Enthalpimetry**

Continuous flow enthalpimetry is used to describe methods wherein a reagent is continuously fed into a flowing analyte stream and the temperature difference is measured before and after a reactor (mixing) chamber. Alternatively, the temperature may be measured in a differential manner between a reference and a reactor chamber. The analyte concentration is directly proportional to the measured temperature difference. Modifications which permit gas analysis are important. An acceptable synonym is *continuous flow enthalpimetric analysis*.