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NOMENCLATURE OF THERMOMETRIC AND ENTHALPIMETRIC METHODS IN CHEMICAL ANALYSIS

(IUPAC Recommendations 1994)

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Nomenclature of thermometric and enthalpimetric methods in chemical analysis (IUPAC Recommendations 1994)

ABSTRACT

This report defines the scope of enthalpimetric analysis within the general field of calorimetry and also delineates it as distinct from the methods of thermal analysis for solid materials. Enthalpimetric analysis is defined as a variant of calorimetry in which the enthalpy change of a chemical reaction is measured in order to perform a relatively rapid quantitative determination of an analyte, and in which at least one reactant is a liquid or solution. Nomenclature is recommended for variations of the methodology in which the reaction is carried out as a titration, as a batch reaction, in flowing streams, or as an injection into flowing streams.

1. INTRODUCTION AND OBJECTIVE

"Enthalpimetry" is a subset of the field of calorimetry. "Calorimetry" is a general term describing any experiment in which heat is measured as some chemical reaction or physical process occurs. "Calorimetry" is derived from the Latin word "calor" meaning heat and the Greek "metron" meaning measure (1). Within the whole of calorimetry are multitudes of experimental arrangements designed to obtain various kinds of information about various kinds of substances. The diversity of types and uses of calorimetry are so great that the systematization of nomenclature is most readily accomplished by considering subfields of the whole. For example, "thermal analysis" is defined as "a group of techniques in which a physical property of a substance and/or its reaction product is measured as a function of temperature while the substance is subjected to a controlled temperature program" (2,3,4). For those techniques in which heat is the measured physical property (i.e. differential thermal analysis, DTA or differential scanning calorimetry, DSC), calorimetry and thermal analysis may be seen to overlap. For thermal analysis, a well-defined nomenclature has already been developed which includes the corresponding calorimetric techniques (2,3).

This particular project is aimed at another subfield of calorimetry. Specifically, it is intended to clarify the nomenclature of the analytical uses of solution calorimetry, which are also known as "enthalpimetry."

The discussion of enthalpimetry requires some review of calorimeter types used for analysis. In simplest terms, a calorimeter is a device for measuring a quantity of heat liberated or absorbed. This quantity of heat is that associated with a particular process. Most commonly, the process is either a chemical reaction or a phase change (which includes mixing or dilution of liquids and dissolution of solutes). Calorimeters differ in the physical principles used to measure this heat and also in the particulars of the type of reaction or process which is monitored. Heat measurement principles are commonly recognized to be of four general types. In addition, four general categories of ways to initiate or control the reaction or process in calorimeters for analytical uses may be delineated.

The quantity of heat may be determined by measurement of a temperature change within the calorimeter if the heat exchange with the environment is minimal, and the "effective heat capacity" of the calorimeter reaction vessel is known. In the "*adiabatic calorimeters*," an outer jacket is maintained at the same temperature as the reaction vessel so that no heat transfer occurs. A more common design are the "*isoperibol calorimeters*", where heat exchange is minimized by insulation of the vessel and placement in a constant-temperature environment (Greek *isos* meaning equal and *peri* meaning around). Another method for heat measurement is by thermal contact of the vessel with a heat sink via a heat flowmeter (usually a thermopile). Calorimeters of this general type are known as "*heat-flow, heat-flux, or heat-conduction calorimeters*." The last arrangement for heat measurement that finds analytical use are the "*power compensation calorimeters*" in which the primary measurement is of the amount of heat energy which must be added to or subtracted from the vessel in order to maintain a constant reference temperature.

Of particular relevance to enthalpimetric analysis are the methods by which the reaction is initiated or controlled. In a *batch* method, a chemical reaction is initiated by the addition of an amount of a reactant or catalyst all at once. Traditionally, a batch method is one in which both reagents are inside the vessel prior to mixing (e.g. one in a glass vial or a dipping pipet). The situation where one reagent (or the analyte test portion or a catalyst) is initially kept outside the vessel may be described by "*batch injection*." In a *titration* method, a chemical reaction occurs as one reagent (the titrant) is added in a continuous manner to a fixed amount of the other reagent in the vessel. Some calorimeters can accommodate gaseous or solid materials in either batch or titration mode. A third method for combining reactants in a calorimeter is by continuous *flowing streams* in a flow-through reaction vessel. The situation where the analyte is injected as a discrete plug into a flowing stream would be described as "*flow injection*", which has the same meaning as in the general methodology called "flow injection analysis" (5,6,7). The use of flow injection to combine analyte and reagents in a calorimeter has found considerable analytical application (8,9,10) including calorimeters in which the flowing stream interacts with a solid or an immobilized catalyst (i.e. an enzyme) on a support in a reactor (11,12,13). A fourth method to initiate or control a reaction or process or phase change in a calorimeter is by a controlled variation of temperature (or sometimes pressure or volume). Within the context of thermal analysis, these are often designated as "*scanning*" methods.

2. DEFINITIONS FOR ENTHALPIMETRIC METHODS

2.1 Enthalpimetric analysis

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. In general, 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 (14).

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" (8) 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" is 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.

Explanatory notes

This restriction of the use of the term enthalpimetry is admittedly arbitrary. In the thermodynamic sense, enthalpimetry means the same thing as (constant-pressure) calorimetry. The use of the terms enthalpimetric analysis and enthalpimetry is justified on historical and current usage, and on subtleties of emphasis.

2.1.1. "Enthalpy" (Greek "enthalpien" meaning heat within) is a term first used in the twentieth century (ca 1927) (15), whereas "calorie" dates back to at least the eighteenth century (1). In the same way, the use of solution calorimetry for chemical analysis (e.g. thermometric titration) dates from the 20th century (16,17), whereas the broader, more fundamental uses of calorimetry are much older.

2.1.2. "Enthalpimetry" was used in much of the early work in this field (18) and is currently a widely used and favored term in many parts of the world.

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

2.1.4. 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.

2.2 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) (18). 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 (19).

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.

2.3 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 a temperature change 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 (20) 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 enthalpy 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.

2.4 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.

2.5 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 (8-13). 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.

2.6 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 (21,22).

An acceptable synonym is continuous flow enthalpimetric analysis.

CONCLUSION

Among the many methods of instrumental analysis available today, a wide variety of properties of chemical substances and their reactions are exploited in order to identify and determine analytes. One of the most general properties is the enthalpy change of a reaction involving the analyte. The detection of this enthalpy change, an extensive property proportional to the amount of analyte reacted, is the basis for the enthalpimetric methods of analysis.

This document defines the scope of enthalpimetric analysis within the more general field of calorimetry and distinguishes it from the methods of thermal analysis for solids. It also provides standardized nomenclature for the basic methods which are in common use (i.e. direct injection enthalpimetry, thermometric titration, flow injection enthalpimetry, and continuous flow enthalpimetry).

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