

COMBINED THERMAL ANALYZER AND X-RAY DIFFRACTOMETER

CROSS REFERENCE TO RELATED APPLICATION

This is a continuation of application Ser. No. 938,682, filed Dec. 5, 1986.

FIELD OF THE INVENTION

This invention relates to a scientific apparatus and a method for observing thermodynamic and structural properties of materials. It particularly concerns an instrument for simultaneous calorimetric and X-ray diffraction analysis.

BACKGROUND OF THE INVENTION

In characterizing the physical and chemical behavior of substances, it is customary to separately investigate both their thermodynamic (e.g., calorimetric) and their structural (e.g. crystallographic) properties.

Thermodynamic properties are commonly determined by differential scanning calorimetry (DSC) and by differential thermal analysis (DTA). Modern DSC and DTA instruments are highly advanced, affording sensitive temperature regulation and measurement, often to a fraction of a Centigrade degree. A sample may be heated rapidly through a wide temperature range, and calorimetric output measured with precision, over a period of a very few minutes.

Crystallographic properties are often studied by X-ray diffraction (XRD) spectrometry. To achieve high resolution, diffraction data have been collected on photographic film, or with scintillation counters. Such procedures are slow, requiring data collection times of thirty minutes or more for each pattern at each temperature. A single scan over a range of temperatures may consume most of a day or longer. Because of the slow data collection times for X-ray diffraction scans, structural and calorimetric data could not be correlated for fast processes. In industrial processes, heat and/or chemical treatments often occur in a matter of a few minutes or seconds (i.e. the extrusion of a polymer or the oxidation of a catalyst). In addition, the equipment for heating samples in X-ray diffraction analysis has been comparatively crude, e.g., uniform sample temperature control within five degrees has been attainable only rarely except near room temperature. For both reasons, rapid scanning, i.e., dynamic reading of a series of X-ray diffraction patterns correlated accurately and simultaneously with temperature rise as a sample is heated, has not been previously practiced.

Instead, the usual approach has been to analyze a sample first by one of the foregoing techniques and then by the other. Data from the two determinations were correlated as best might be, to elucidate as far as possible the thermostructural behavior of the sample. However, due to the differences in sample heating conditions and sample size, and in the data collection times between DSC and conventional XRD, the diffraction and calorimetric data did not correlate well when trying to assign an observed structural change to a particular calorimetric event. In applying this method to multi-component samples, separate physicochemical phenomena occurring at closely spaced temperatures were often missed or misinterpreted as were indications of

transitory species and irreversible phase changes occurring over a period of a minute or two.

More recently, one aspect of this situation has been improved. Position sensitive detectors have been developed as X-ray detectors, dramatically increasing the speed of acquiring diffraction data. With them, the time scale for X-ray diffraction analysis can be shortened to be compatible with that of differential thermal analysis and differential scanning calorimetry.

The present invention takes advantage of this improvement and provides a workable instrument and method for simultaneous dynamic observation of thermodynamic and structural properties of a sample undergoing temperature and/or environmental change.

SUMMARY OF THE INVENTION

The instrument of the invention includes in combination both an X-ray diffractometer and a thermal analyzer (either a differential scanning calorimeter or a differential thermal analyzer) mounted to cooperate and simultaneously coact on the same sample undergoing analysis. The diffractometer includes a source of an X-ray beam directed to impinge on a sample also being acted upon and observed for determination of certain thermodynamic properties, and a rapid position sensitive detector to receive radiation diffracted from the sample to determine structural properties. The thermal analyzer includes within a sample holder assembly, a sample holder on or by which means the sample is positioned and retained for the joint analysis. The sample holder assembly has an inlet port or X-ray transparent window positioned to allow the diffractometer X-ray beam to strike the sample in the holder and an outlet slit or window to allow passage of diffracted radiation to the X-ray detector. The analyzer also includes control means for changing the temperature of the sample in the holder and means for observing the thermodynamic behavior of the sample during such change.

The X-ray source preferably provides a focused monochromatic beam. Advantageously, it is a line source equipped with a Guinier diffraction system and a curved focusing monochromator. The source and the sample holder (and the surrounding enclosure) are arranged geometrically so that a sample in the holder lies at a point along the focusing circle of the diffractometer.

The X-ray detector is preferably a position-sensitive proportional counter mounted for movement about the focusing circle of the diffractometer with the sensitive element placed along the arc of the circle. The detector is connected to electronic readout circuitry. This may include a multichannel analyzer with a display terminal or recorder to indicate numerically and graphically the positions and intensities of the lines forming the X-ray diffraction pattern.

The thermal analyzer is preferably a differential scanning calorimeter provided with electronic readout circuitry to display and record both the temperature of the sample throughout analysis and the existence and magnitude of calorimetric events occurring in the sample. The circuitry also contains means for controlling the temperature of the sample in the holder. Beneficially, this means is programmable to increase, decrease or hold the temperature.

As a non-limiting example, the sample holder assembly (sometimes referred to as the specimen holder assembly or cell) may comprise a protective enclosure, conveniently a metal block with a cover to seal the