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ADVANCED SEDEX (SENSITIVE DETECTOR OF EXOTHERMIC PROCESSES)

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ABSTRACT

The instrument described is suitable for the investigation of the thermal behaviour of substances and reaction mixtures under production conformable conditions; this is made possible by the sophisticated design of the sample chamber: easy stirring of the samples, measuring under any gas atmosphere and while bubbling gas through the sample, choice of the sample container and visual observation during the measurement. The control device allows the choice of one of three operational modes: constant temperature, linear increase in temperature, and adiabatic control; this permits the application of the SEDEX apparatus for a variety of methods including dynamic scanning, isoperibolic measurements, and (quasi) adiabatic studies.

INTRODUCTION

Today a whole series of measuring methods and devices is available for investigating the thermal behaviour of substances, such as DSC, DTA, TG, heat accumulation methods, Sikarex, dynamic decomposition test, long-term decomposition test block, etc. [1–3]. In the chemical industry, in view of the immense potential dangers which a heat explosion represents or contains, the precise investigation of the thermal sensitivity of systems of substances under industrial operating conditions has assumed particular importance. For this reason, the following particular requirements must be met by a device used for such investigations.

(a) High sensitivity.

(b) Mode of operation conformable to plant conditions:

(1) simple stirring of test samples;

(2) possibility of using any desired sample container;

(3) investigations of samples under any desired gas or while bubbling gas through the sample;

(4) visual observation of the samples during the investigation.

(c) Economy:

(1) low price of the apparatus;

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(2) simultaneous measurement of several samples;
(3) prompt and reliable results.

(d) Simplicity and ease:
(1) simple in function and easy to operate;
(2) objective and simple interpretation of the results.

As none of the devices presently available fulfils the above conditions, the impetus was given to develop a new type of apparatus which takes into consideration all of these requirements of the chemical industry: the SEDEX [4,5].

DESCRIPTION

The SEDEX is essentially composed of three parts (Fig. 1):

(a) heatable chamber with circulating gas, sample holders and stirrer, which together constitutes the oven module;

(b) control module with possibility of maintaining constant temperature, regulating a linear rise in temperature or introducing adiabatic temperature control;

(c) recording device.

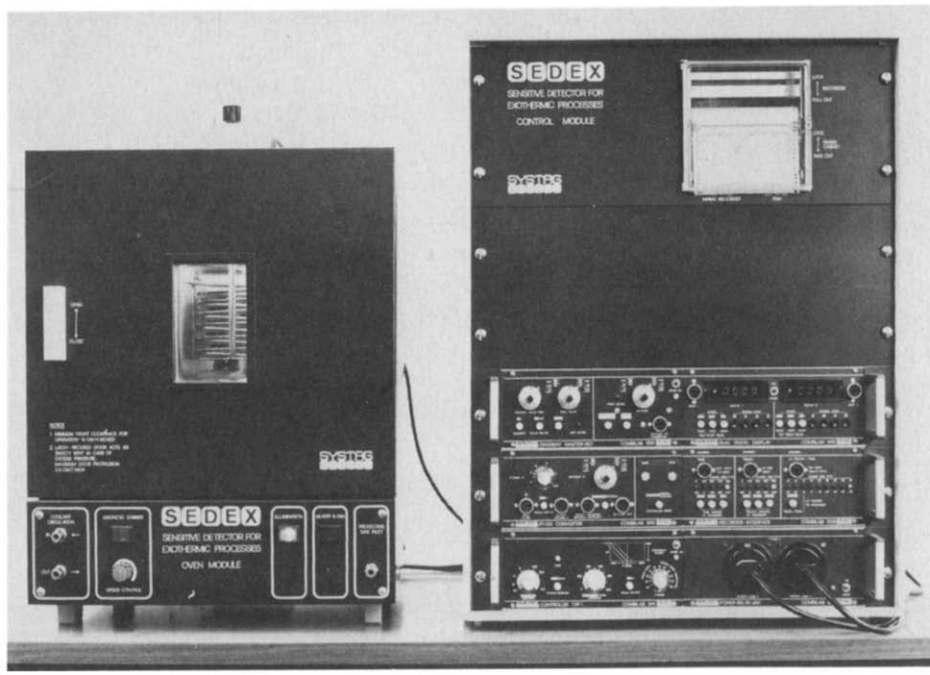

Fig. 1. SEDEX—the overall view.

Oven module (Fig. 2)

One of the most important prerequisites of an oven suitable for the intended purposes is the homogeneous spatial distribution of the temperature within its working area. In the SEDEX this is assured by a heating system consisting of heating and cooling coils, and a fan. The oven housing is made of stainless steel with asbestos insulation. The sample holder inside of the oven is capable of holding two sample containers; this permits two samples to be investigated simultaneously. The sample containers are normally beakers of 50 ml capacity, but it is quite possible to use other containers, if this should prove necessary or desirable. A Dewar flask, an autoclave and a sulphonating flask have been successfully tested for this purpose. The removable tray under the samples prevents liquids or molten substances from getting into the interior of the apparatus and permits easy cleaning. In the front panel (door) of the apparatus is a bullet-proof window.

Fig. 2. Oven module.

This permits visual observation of the samples during measurements and facilitates the evaluation of the measurements (visible effects such as melting, change of colour, gas or smoke development, boiling, glowing, etc.).

The measurements can be carried out either in air or under any desired gaseous atmosphere. Inert conditions are best achieved by using nitrogen. For this purpose, the oven is fitted with two nipples, one serving to introduce the gas and the other for connecting the exhaust pipe. A flow rate of ca. 10 l min^{-1} assures an adequate elimination of atmospheric oxygen (oxygen residue approx. 1 vol.%) without disturbing the uniform distribution of temperature within the oven.

The cover of the oven is removable and can be equipped with openings as desired for the temperature sensors, stirrer shafts, pipes for gases and educts, reflux cooler, etc. With a few interchangeable covers an exceptional degree of flexibility can be achieved. Stirring is not necessary in every case, but it is especially recommended when suspensions or emulsions are to be investigated. For this purpose a normal glass stirrer is used which is driven by a laboratory motor of the usual type with a variable stirring speed. Another possible method of stirring is described below.

Control module

To control the temperature in the SEDEX oven, devices of the "Combilab" series of SYSTAG [6] are used. The Combilab system is designed according to the building-block principle, which makes it possible to assemble a tailor-made measuring and controlling system adapted to any specific requirement, or to expand an existing system as desired, according to changes or new requirements. All outputs are located on the front panels for recording purposes. Only a few basic components are equipped with a power supply unit and the coordination of signals and power supply for the other components takes place via a party line. The electronic equipment of the SEDEX system largely depends on the investigations for which it is to be used and the requirements as to the ease of operation and control. The typical building-block combination to control the linear increase of the temperature is illustrated in Fig. 1.

Normal commercial Pt-100 sensors are used for measuring the temperature.

Recording device

The oven and sample temperature as well as the difference between these temperatures are to be registered. The minimum equipment is a three-channel recorder with measurement ranges of 100 mV and 1 V and a variable chart speed in the range of 1–6 cm h^{-1}. In order to ensure a trouble-free evaluation of the measurements, it is advantageous to use a dot printing

recorder as the time lag of the signals with a pen recorder makes the evaluation more difficult.

The use of any other data acquisition and processing system via an appropriate interface is, of course, possible (such as a minicomputer of usual type).

EXAMPLES OF USES

The sophisticated design of the oven and the flexibility of the Combilab system permit the versatile use of the SEDEX apparatus. Therefore, in the following sections only the typical possible uses of the device will be described. Other working procedures can be employed with a simple addition to the control system and its appropriate extension.

Determination of initial temperature of exothermic processes

The sample is prepared in a suitable receptacle, e.g., a 50-ml glass beaker, and placed in the SEDEX oven. The temperature in the oven is raised in a linear fashion, typically at a rate of 30 °C h^{-1}. The temperature of the heating medium and of the sample is measured by Pt-100 sensors. The signals of the sensors are converted into an electrical impulse by means of the dual Pt-100 convertor and registered on a three-channel recorder. With suitable wiring of the outlets from this dual convertor the difference between these temperatures is simultaneously generated and registered on the same recorder with a much greater (normally 10 times) sensitivity. If no process with heat effects takes place in the sample, the difference between the two temperatures remains constant. The temperature at which the difference begins to decrease is the initial temperature of an exothermic process. Conversely, the temperature at which the difference begins to increase is the initial temperature of an endothermic change. The combination of a heating rate of 30 °C h^{-1} and a chart speed of 2 cm h^{-1} permits the reliable registering of a change of temperature difference by 1 °C h^{-1} which, with a sample weight of about 30 g, corresponds to a detection sensitivity of no less than 0.5 W kg^{-1} test material. In most cases this arrangement has proved to be the most favourable one, although another combination of sensitivity and chart speed is quite possible.

The evaluation takes place graphically and is shown directly on the recording paper. It is extremely simple and illustrative. An example using 3-nitroaniline is shown in Fig. 3.

The initial temperatures of certain substances determined with the SEDEX method clearly demonstrate the outstanding sensitivity of this apparatus as compared with values found by DSC (Table 1).

Mini-autoclave with stirrer

Pressure autoclaves are necessary when endothermic evaporation effects need to be suppressed. A considerable disadvantage of former methods for investigating thermal stability under pressure was the inability to stir the sample. When investigating multiphase systems, measurements taken without stirring the sample are incorrect and often meaningless, e.g., when the phases of an emulsion are completely separated or when there is sedimentation of the solids in a suspension which is not stirred. This problem can be solved by using the SEDEX, which is fitted with a magnetic stirrer. A strong magnet fixed to a drive shaft is located immediately under the floor of the oven. The magnet is powered by an electric motor with variable speed. The magnetic stirring rod located in the mini-autoclave is driven by the rotating magnet and acts as the stirrer.

TABLE 1

Initial temperatures of certain substances with the SEDEX method compared to DSC

Substance	Initial temperature (°C)	
	DSC	SEDEX
p-Xylylchloride with 0.02% Fe	80	55
1-Nitroanthrachinone	380	295
1,5-Dinitroanthrachinone	370	315
Dodecylnitrite	145	115

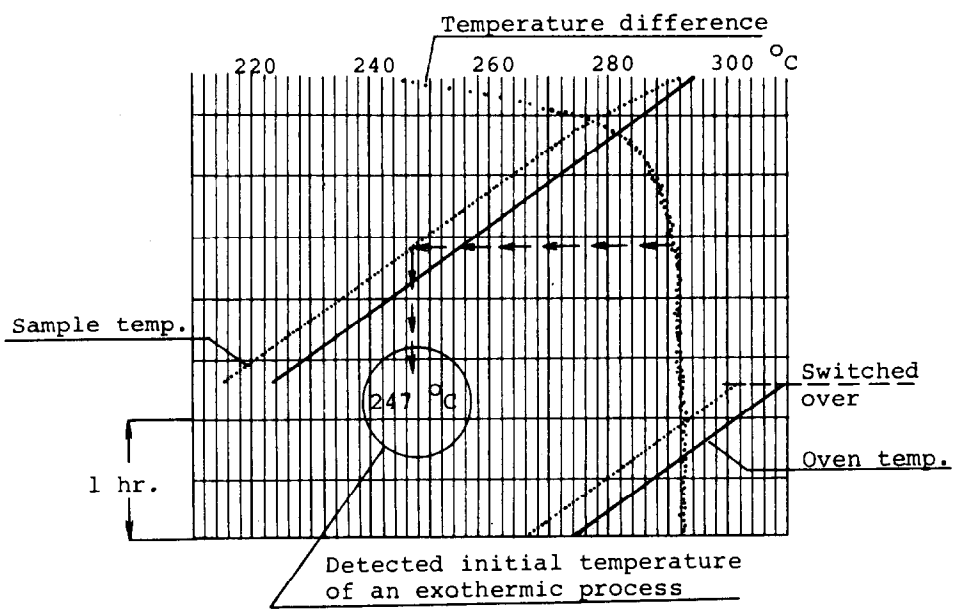

Fig. 3. Initial temperature of exothermic decomposition of 3-nitroaniline.

When measuring corrosive mixtures, the walls of the mini-autoclave must be protected. This is achieved by a fitted glass lining and the probe for the temperature sensor is shielded with a specially designed protective tube of glass. This combination permits investigations which were previously not possible, such as the study of corrosive suspensions under pressure, with stirring (Fig. 4).

Besides the usual opening for the temperature sensors, the cover plate of the oven also has an opening for the relief tube of the mini-autoclave. This arrangement ensures that in a case when the bursting disk ruptures, the contents of the mini-autoclave will not penetrate into the interior of the SEDEX oven but, instead, will be ejected from the apparatus. The outlet of the relief tube on the cover plate can also be covered with a stainless-steel collector with a volume of ~ 1 l. The tightly fastened container prevents the contamination of the environment by the ejected material when the bursting disk ruptures.

One of the most important characteristics of the equipment is its high sensitivity. This is especially manifested in the determination of the initial temperatures of exothermic processes. Table 2 provides an impressive demonstration of this sensitivity on several examples of reaction mixtures. It shows the results of measurements in the SEDEX mini-autoclave as compared with the results of the mini-autoclave according to Ciba-Geigy-Kühner. The differences found were from 30 to 45 °C.

The most important features and properties of this equipment are listed below.

(a) Simple stirring of the samples in the mini-autoclave.

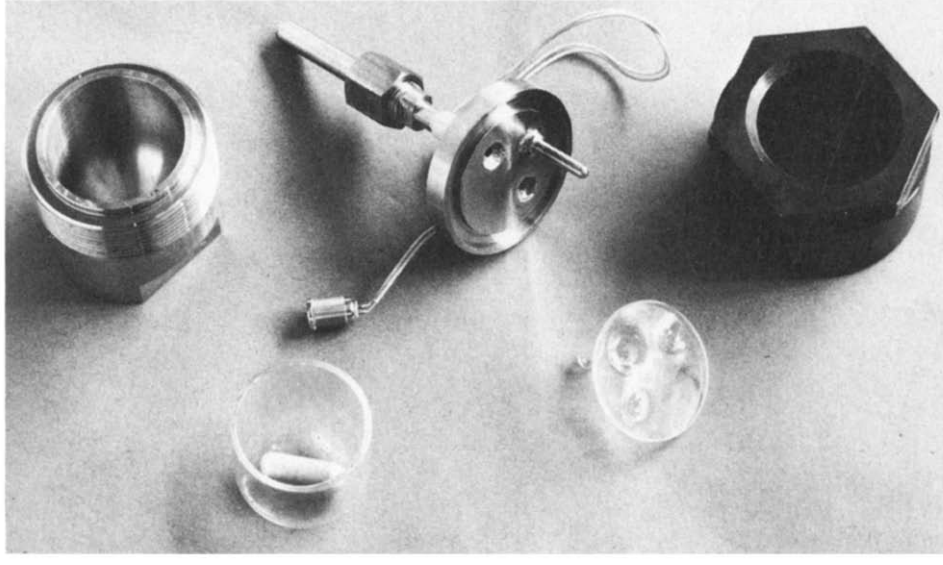

Fig. 4. Stirrable mini-autoclave of 50 ml capacity with protective glass inserts.

(b) Problem-free operation at pressures up to 350 bar and temperatures up to 350 °C.

(c) Effective stirring of thick suspensions and emulsions or corrosive liquids of high viscosity.

(d) Use of autoclaves of different designs and sizes.

(e) Carrying out of pressure reactions, i.e., informative experiments without great expenditure.

(f) Semi-quantitative or quantitative estimation of heat effects.

(g) Simple design, thus, trouble-free operation.

SEDEX/ADOPT (ADiabatic OPTion)

Investigations of substances and mixtures under adiabatic conditions, i.e., without any addition or removal of heat, are of particular interest and have therefore been intensively studied [7,8]. Measurements of this type simulate conditions, e.g., in an uncooled kettle where stirring is stopped, or in a large storage container, and thus help to estimate the danger potential of these systems. Adiabatic investigations can be carried out rationally and advantageously in the SEDEX. Thanks to the Combilab modular building-block system, the necessary expansion of the control system is simple and unproblematical.

The most notable disadvantage of most adiabatic calorimeters is the lack of a compensation for the heat capacity of the sample container. In the SEDEX system, since the typical working amounts are 20–40 g, the heat capacity of the sample container (typically about 40 J K^{-1}) is therefore not negligible in comparison with that of the sample, so that an automatic compensation was considered necessary. In the SEDEX, the sample container for adiabatic measurements is equipped with a heating element. The temperature of the sample is taken and relayed to the automatic compensator (Combilab SIKADIFF), which provides the first derivative of the actual rise in temperature in the sample and controls the rate of heating of the sample container from a precision power supply. Based on the example of

TABLE 2

Initial temperatures of exothermic processes of certain substances with the SEDEX method compared to Ciba-Geigy-Kühner

Reaction mixture	Temperature at beginning of 1st exothermic reaction (°C)	
	Ciba-Geigy-Kühner	SEDEX
1-Methyl-2-nitrobenzene-4-sulphonic acid	215	170
Phenol resin for finishing cellulose	170	130
2-Amino-1-methyl-4-nitrobenzene	180	150

the adiabatic temperature rise in the decomposition of decylnitrite, measured in the SEDEX first without and then with automatic compensation, the importance of taking into account the heat capacity of the sample container in adiabatic measurements becomes clearly evident (Fig. 5).

The SEDEX/ADOPT configuration can also be used to carry out over-adiabatic calorimetry (OAC). This method was developed for the determination of the heat of reaction of slow and/or weak exothermic processes within a reasonably short time. The name OAC expresses the nature of the method: reaction under quasiadiabatic conditions but at higher temperatures than ideal adiabatic in order to shorten the reaction times. The measurements can advantageously be carried out in a SEDEX oven. The reaction mixture in a suitable receptacle, preferably while being stirred, is heated by an electric heater fed by a constant power source. The temperature in the reaction mixture is measured and its first derivative with respect to time is formed

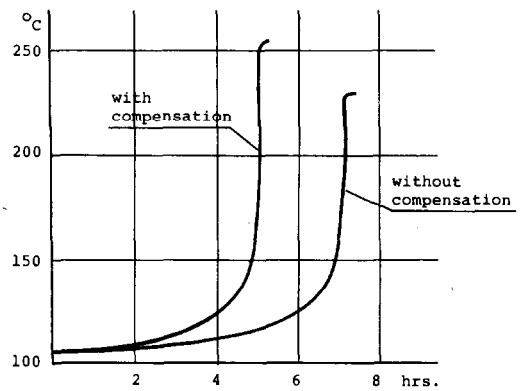

Fig. 5. Adiabatic course of the temperature in the decomposition of decylnitrite: influence of the heat capacity of the container.

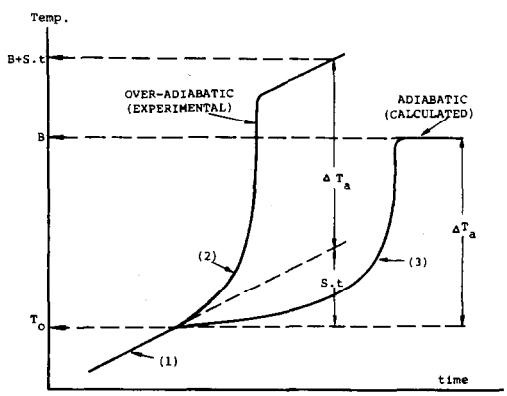

Fig. 6. Principle of over-adiabatic calorimetry. For explanations of symbols and details see ref. 9.

and recorded. If no process with heat effects takes place in the reaction mixture, the temperature rises in a linear fashion, i.e., the first derivative remains constant. At the temperature at which the reaction starts producing its own heat, the temperature rise will be accelerated and can be described by a modified Arrhenius equation. One of the parameters of this equation can be read from the temperature recording and used directly for the determination of the heat of reaction, the remaining two parameters can be estimated from the dT/dt data by a regression analysis and used for the calculation of the course of the process under adiabatic conditions (Fig. 6). Thus, the OAC method allows the determination of the heat of reaction and kinetic parameters especially of weak and/or slow exothermic processes with acceptable precision and with moderately-priced equipment. For details see ref. 9.

DISCUSSION

In the SEDEX apparatus the chemical industry has at its disposal an exceptionally versatile device for investigating the thermal stability and other properties of substances under industrial operating conditions. The possibilities of this apparatus are not limited merely to the working methods described above. Numerous other possibilities are open to the user of this system: isothermic measurements, heat accumulation studies, Temper method [10], etc.

In addition to its flexibility, the SEDEX possesses other advantages such as the following.

(a) High sensitivity: about 0.5 W kg^{-1} test material.

(b) Possibility of stirring: the samples can be stirred with a normal laboratory stirrer or a magnetic stirrer.

(c) Measurements under a protective atmosphere: investigations under a protective gas can be performed very easily.

(d) Addition of substances: it is a simple matter to add solid, liquid or gaseous educts or additional components by means of an inlet pipe, even during the investigation.

(e) Flexibility with respect to sample container: any desired receptacle can be used, e.g., a mini-autoclave or a Dewar vessel.

(f) Observation of visible effects: the samples can be visually observed during the investigation. The observation of effects such as melting, change of colour, gas or smoke development, boiling, glowing, etc., facilitates the evaluation and interpretation of the measured results.

(g) Simplicity: the operation of the apparatus requires no special training and the device does not need to be corrected or adjusted during measurements. The evaluation of the experimental results is easy and objective.

(h) Precision and reliability: the measured values agree with the results of

much more elaborate methods (with respect to time, price and labour-intensiveness).

(i) Ease of maintenance: substances which escape from the sample containers are collected in the protective tray and do not impair the proper functioning of the apparatus.

(j) Hygiene: the device is enclosed and any potentially toxic substances remain within the test chamber. Thus, these substances can be tested for toxicity after or during the passing of a gas through the chamber.

REFERENCES

1 A.V. Zatka, Thermochim. Acta, 28 (1979) 7.
2 L. Hub, Dissertation No. 5577, ETH Zurich, 1975.
3 T. Grewer, Chem.-Ing.-Tech., 51 (1979) 928.
4 J. Hakl, Thermochim. Acta, 38 (1980) 253.
5 J. Hakl, Chem. Tech., 8 (1979) 505.
6 SYSTAG Inc., Bahnhofstr. 76, 8033 Rueschlikon, Switzerland.
7 W. Frankvoort and W.R. Dammers, Thermochim. Acta, 11 (1975) 5.
8 D.I. Townsend and J.C. Tou, Thermochim. Acta, 37 (1980) 1.
9 J. Hakl, Proc. 10th NATAS Conf., 1980, 281.
10 G. Hentze, Rapperswiller TA-Symposium, 1979, Switzerland.