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IDENTIFICATION OF SOME SWEETENING AGENTS BY THERMAL ANALYSIS

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The thermal behaviours of some artificial sweetening agents — sodium cyclamate, saccharine and sorbitol — were studied by means of a complex thermal method.

The quite different thermal behaviours of the different sweeteners are utilized for their identification. An endothermic peak is seen in the DTA curve at about 386° and 94° for saccharine and sorbitol, respectively, which is not accompanied by a weight loss. In the case of sodium cyclamate a characteristic exothermic peak followed by an endothermic one is detected. A semiquantitative method for the determination of sodium cyclamate is described.

Until recently, three artificial sweeteners and their salts were permitted in foods: saccharine (o-benzoic sulphimide) and its sodium, calcium and ammonium salts, sorbitol (hexahydric alcohol) and the cyclamates (salts of cyclohexylsulphamic acid). The importance of these sweetening agents is that they are generally regarded as safe. Their use has been proposed in canned fruit, for which a Federal Standard of identity was issued [1]. Most of these sweeteners are also common ingredients in various pharmaceutical products.

Saccharine and its salts (as widely-used artificial sweeteners) have been subjected to much work for their estimation [2, 3]; some of the methods depend upon the presence of the imide group [4, 5].

Several procedures have been described in the literature for the determination of sorbitol, but most of them either lack specificity or ease of use [6]. Some of the methods which have been reported for the quantitative estimation of sorbitol depend on its oxidation [7] or complexation [8]. In addition, spectrophotometric [9], gravimetric [10] and polarimetric [11] methods have been described.

Sodium cyclamate has been determined by titration in aqueous [12] and non-aqueous media [13]. Gravimetric [14], complexometric [15] and spectrophotometric [16] methods have also been reported.

Mitchell [17] has worked out a rapid paper-chromatographic method for the simultaneous detection of these artificial sweeteners.

In the present work a simple thermal method for the identification and detection of saccharine, sorbitol and sodium cyclamate, and a semiquantitative determination of sodium cyclamate, are described.

Experimental

Materials and apparatus

Saccharine sodium: dried at 110° for 4 hours. The purity was checked by the method of the United States Pharmacopoeia XVI, and was found to be 98.2%.

Sorbitol: The purity was checked by the B. P. 1973 method, and was found to be 99.97%.

Sodium cyclamate: The purity was checked by the B. P. 1968 method, and was found to be 100%.

The measurements were made with a derivatograph (MOM, Hungary) under the following conditions: Sample size: 100 mg. In the case of a mixture, equal portions (i.e. 33.3 mg of each) were taken. Heating rate: 5°/min. Temperature was increased linearly from 25 up to 500°. Reference material: Al_2O_3.

Quantitative determination of sodium cyclamate

Various amounts of sodium cyclamate (5–30 mg) were treated in the derivatograph under the previous conditions.

Results

Table 1 indicates the different reactions occurring in the temperature range 25–500°, with regard to their beginning, ending and the percentage weight loss in every reaction, together with the temperatures of the endothermic peaks of the samples examined.

Table 1

Thermal reactions of sweeteners together with the temperatures of their endothermic and exothermic peaks

Sample	Thermal reaction		Total weight loss, %	Temperatures, °C of	
	Temperature start	°C end		endothermic peaks	exothermic peaks
Saccharine sodium	442	508	32	386	500
Sorbitol	254	385	88.4	94.350	—
Sodium cyclamate	225	356	52.8	324.403	260

Figures 1–4 show the thermal curves of the dried samples of saccharine, sorbitol, sodium cyclamate and a mixture of equal parts of them, respectively.

The relation between different quantities of sodium cyclamate and the area under its characteristic exothermic peak, which has its maximum at 260°, is shown in Fig. 5.

The thermal curves of saccharine (Fig. 1) indicate that no loss in weight occurs till 442°, where a reaction starts. This reaction is exothermic, with its peak temperature at 500°. An endothermic peak is also noticed (DTA curve), having its maximum at 386°, which is not accompanied by weight loss.

In the DTA curve of sorbitol (Fig. 2), the large endothermic peak accompanying the main reaction shows another small peak temperature at 340°. The DTG curve also shows that the reaction may consist of two stages, the first one ending at 346° with 65% weight loss.

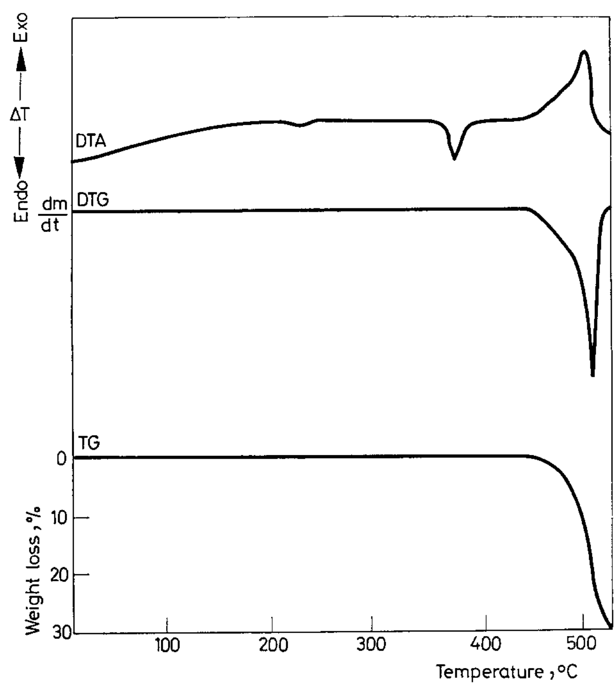

Fig. 1. Thermoanalytical curves of saccharine

As regards sodium cyclamate, there is an increase in weight of the sample of about 1%, starting from 190° and ending at 225°. The main reaction is found to consist of two distinct stages (Fig. 3), the first and smaller one of them ending at 282° with about 10% weight loss. This stage is accompanied by an exothermic peak, while that of the other is endothermic in nature.

With regard to the thermal stabilities of these compounds, from the thermoanalytical curves saccharine sodium is found to be the most stable. It starts to lose weight (chemically decomposes) at 442° (the end of this reaction was determined from an experiment carried out on a sample of saccharine sodium heated to 1000°). Sorbitol starts to decompose at 254°. The least stable of the examined compounds is sodium cyclamate, which starts to decompose at 190°.

As shown in Table 1, the endothermic peaks occurring at 386 and 94° for saccharine sodium and sorbitol, respectively, are not accompanied by weight loss and may be due to phase-transitions of these compounds.

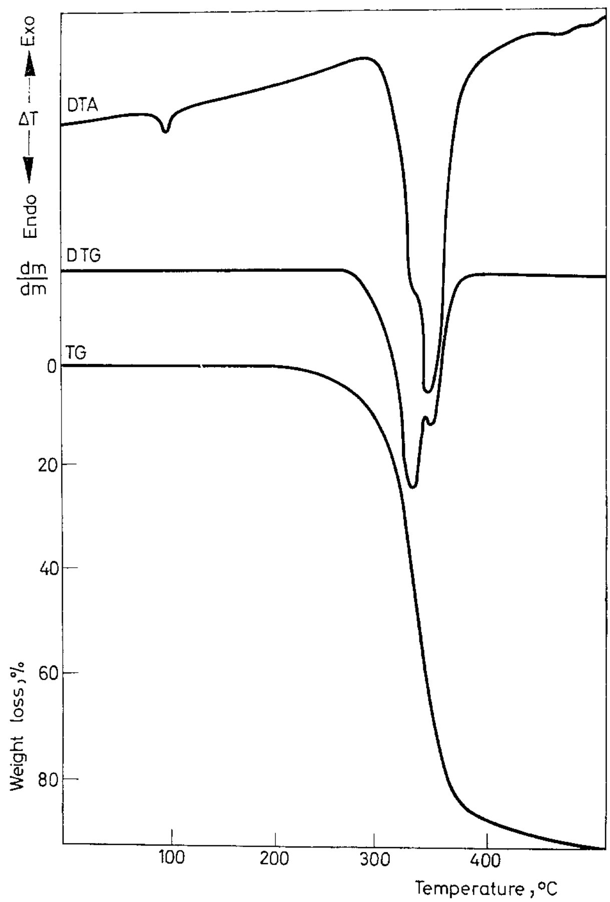

Fig. 2. Thermoanalytical curves of sorbitol

Thermal analysis is thus useful as a means of identification.

For saccharine sodium no changes are seen in the DTG and TG curves up to 442°. Sorbitol can be characterized by the presence of the endothermic peak in its DTA curve, with its maximum at the relatively low temperature of 94°.

Sodium cyclamate is distinctly characterized by the presence of the exothermic peak having its maximum at 260°. In the case of sorbitol no exothermic peak is detected in the temperature range of interest, while saccharine sodium has an exothermic peak at about 500°, which is very far from 260°.

On examination of a mixture of equal amounts of the above sweeteners (Fig. 4), the clearest peak seen is that of sodium cyclamate, which is exothermic in nature. The endothermic peaks of saccharine sodium and sorbitol at 386 and 94°, respectively, are also detected.

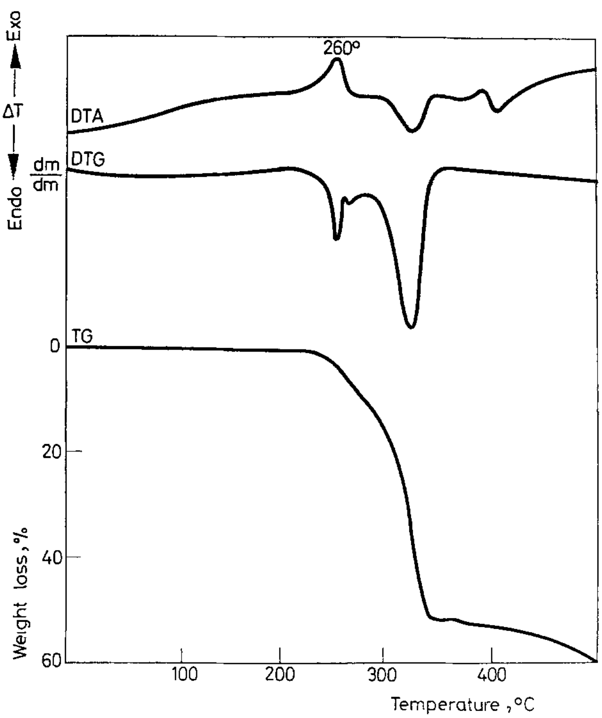

Fig. 3. Thermoanalytical curves of sodium cyclamate

These peaks could be seen in the DTA curve, being present in temperature ranges far from those of the other reactions.

The two peaks for saccharine sodium and sorbitol (at 386 and 94°) are displayed very weakly in the thermal curves of the mixture; this may be due to the reaction of these compounds with each other as a result of the heating. Accordingly, in the mixture it is virtually only possible to detect sodium cyclamate.

From the above conclusions, the exothermic peak of sodium cyclamate having its maximum at 260° promises to be useful for semiquantitative determination besides its importance in the qualitative detection of the compound.

The linear relation between the area under this exothermic peak, as measured for the original curve, and the amount of sodium cyclamate (Fig. 5) introduces a novel method for its determination, which is simple, accurate and of good reproducibility (Table 2).

The method is advantageous as it is simple, no reagents or chemical treatment being needed, and it is also rapid, since a complete experiment can be run within 100 minutes and the qualitative and semiquantitative determinations performed. Further, it reveals whether sodium cyclamate was present alone or in a mixture with the other sweeteners. The time of the experiment can be further reduced if

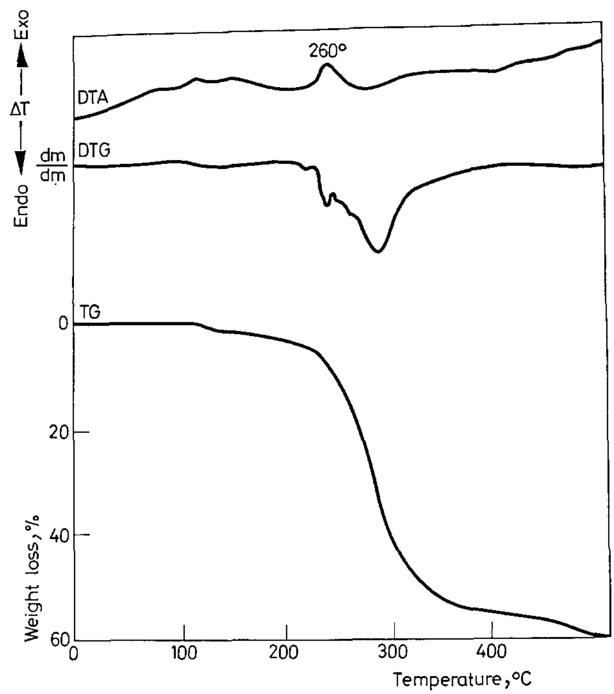

Fig. 4. Thermoanalytical curves of mixture 1 : 1 : 1 of saccharine sorbitol and sodium cyclamate

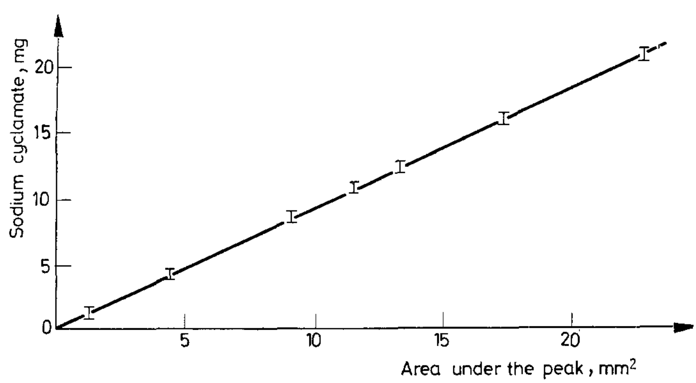

Fig. 5. Calibration curve of sodium cyclamate

Table 2

Determination of sodium cyclamate by the new derivatographic method

	Amount taken, mg	Amount found, mg	Recovery, %
1	5	5.1	102
2	7	7.0	100
3	9	9.2	102.8
4	10	10.1	101
5	12	12.0	100
6	13	13.1	100.8
7	14	14.2	101.4
8	16	16.0	100
9	17	17.3	101.7
10	18.6	18.6	100

Mean recovery = 100.97 ± 0.71
($P = 0.05$).

the measurement is run only up to the end of the exothermic peak of interest (about 300°).

If sodium cyclamate is found in a pharmaceutical preparation, it can be determined after being extracted [18]. In the presence of saccharine sodium and/or sorbitol, sodium cyclamate can be detected (as described previously), but for quantitative determination the results are low. The recommended procedure in this case is to separate it first by a suitable method [18].

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RÉSUMÉ — Le comportement thermique complexe de quelques édulcorants artificiels a été étudié: le cyclamate de sodium, la saccharine et le sorbitol.

Le comportement thermique tout à fait différent de ces divers édulcorants est utilisé pour les identifier. Un pic endothermique apparaît à environ 386° sur les courbes ATD de la saccharine et à 94° pour le sorbitol. Cet effet n'est pas accompagné d'une perte de poids. Dans le cas du cyclamate de sodium, on décèle un pic exothermique caractéristique suivi d'un pic endothermique. Une méthode a été mise au point pour le dosage semi-quantitatif du cyclamate de sodium.

ZUSAMMENFASSUNG — Das thermische Verhalten einiger künstlicher Süßmittel — Natriumcyclamat, Saccharin und Sorbit — wurde durch eine komplexe thermische Methode untersucht.

Das sehr unterschiedliche thermische Verhalten der verschiedenen Süßmittel wurde zu ihrer Identifizierung herangezogen. Ein endothermer Peak wurde in der DTA-Kurve bei etwa 386° für Saccharin und bei 94° für Sorbit beobachtet, der nicht von Gewichtsverlust begleitet wird. Im Falle von Natriumcyclamat wurde ein charakteristischer exothermer Peak mit nachfolgendem endothermen Verlauf nachgewiesen. Eine halbquantitative Methode wurde zur Bestimmung von Natriumcyclamat entwickelt.

Резюме — С помощью комплексного термического метода изучено термическое поведение синтезированных сахаристых веществ цикламата натрия, сахарина и сорбитола. Различное термическое поведение исследованных соединений использовали для их идентификации. На кривых ДТА около 386° и 94°, соответственно для сахарина и сорбитола, проявляется эндотермический пик не сопровождающийся потерей веса. В случае цикламата натрия проявляется характерный экзотермический пик, за которым следует эндотермический пик. Разработан полуколичественный метод определения цикламата натрия.