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APPLICATION OF THE DIRECT INJECTION ENTHALPIMETRY /DIE/ IN THE AGRICULTURAL INDUSTRY

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ABSTRACT

A routine analysis was used to determine the urea content in different types of fodder and additives by the DIE method.

INTRODUCTION

The microorganism living in the intestines of ruminants is able to convert non-protein nitrogen /NPN/ into protein. Urea with high N content plays an prominent role as a source of protein.

However too much of urea acts as poison, thus it has to be applied in low concentration or in the form of products of slow decomposition /having retarding effect/. Thus mixed feeds prepared for ruminants contain either free urea or bound /e.g. starch-urea complex/ urea.

Patents protect the technologies of the manufacture of complexes serving the retardation of urea decomposition. Partly DSC /1/ method, partly the investigation of the rate of dissolution is being used to determine the effect of urea preparations /2/. X-ray diffraction can also be used to study structural changes.

A thermometric method has been elaborated for rapid, serial determination of bound, free or total urea content.

Standards valid for the determination of the urea content of fodders /3/ can only measure the total urea content, thus here only the related part of the new method is described.

Thermometric method is based on the observation, that reaction -heat between urea and hypobromite is fairly high /4/.

$$C(=O)(NH_2)_2 + 3\ BrO^- \rightleftharpoons N_2 + CO_2 + 3\ Br^- + 2\ H_2O \quad \Delta H = -281\ kJ/mol$$

Due to the instability of the reagent, the application of the DIE method is evident /5/.

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Should the fodder contain urea in a mechanically mixed form, with solution taking place in seconds, invers DIE method can be applied /6/. This can be used with some urea complexes also, which- although having in-vivo retarding effect-decomposes is water solutions immediately, and the small endotherm dissociation heat of the complex is by several orders smaller than the reaction heat of hypobromite-urea. In both cases it is important to determine what quantity of the sample would truly represent the composition of the fodder to be investigated, and whether the other components could take part in the redox reaction.

MEASURING METHODS

Reagent: 1 M NaOBr solution /R/
Urea stock solution 1 mg/ml
Samples: Various types of industrial feedingstuff preparations
Instrument: solution calorimeter made in Hungary
Radelkis OH-814 recorder.

The calorimeter was used in two ways:

The traditional way: the sample solution was introduced into the measuring cell, the reagent into the immersion pipette /7/.
Inverse way: the reagent was introduced into the measuring cell, and defined quantities of the solid sample from a thermostated sample-holder in series, with the heat capacity /reagent level/ kept on the constant value.

In both cases magnetic mixing was applied, and the heat changes were sensed by a thermistor attached to a Wheatstone bridge, and the signals were recorded on a digital indicator and/or recorder.
Determination: Every case when urea has not been solved instantaneously or when the fodder was very rough, fibrous, dis-homogenous, 10 g of the fodder was used to prepare a solution in accordance to the standard so, that the expected urea concentration should be around 1 mg/ml. Of this 10 ml was diluted to 100 ml, and poured into the measuring cell. 5 ml of the reagent was taken into the submerged pipette. After the temperature equilibrium was reached the reagent was added. Sensitivity: 200 mV where the total deflection of recorder corresponds $\Delta T \approx 0.5\ ^{o}C$. One investigation lasted about 15 minutes. Three parallel determinations were made.

Among the conditions described above 3 parallel investigations

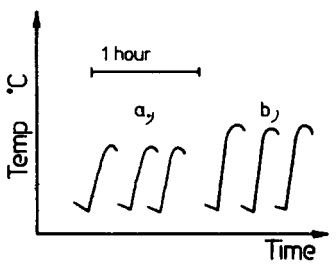
were made with 10 ml of the urea stock solution. /Fig 1./

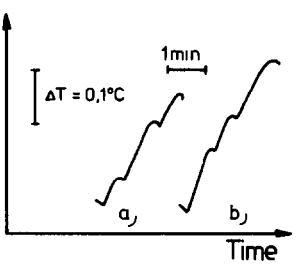
If the urea % did not correspond with the value of the model, or with the method of the standard, blank measurements were also made: every component of the fodder was measured by R, and the one that produced reaction heat was used for correction. Another method to avoid disturbing effects was to draw the diagram with standard addition.

If urea was in a free form in the fodder or in a fast decomposing complex, and was of in a homogenous, fine milled form so that 100 or 200 mg of it could reliably represent the sample, invers-DIE method was used.

Determination: 20 ml from R was diluted to 100 ml and poured into the measuring cell. From the temperated solid sample precisely weighed portions were added which were expected to contain about 10 mg urea each into the measuring cell. Three measurements were made.

The results were related to the units of mass, and their average was taken. The results of the measurements were related to dry-dilution urea. The scale deflection was read off after 1 to 3 minutes. /Fig 2./





Enthalpograms

Fig.1. of a./sample solution
b./urea stock solution

Fig.2. of a./solid samples
b./urea

RESULTS AND DISCUSSION

The table presents the results ontained by various methods.

Commercial names	urea content %			
	nominal	solid	solution	standard
urebetin		6.4	6.5	6,1
bentokarb model	36.0	33.0	37,0	35.7
cattle concentrate		9.3	9.0	9.2
szemakarb		8.7	8.0	8.2
urevitid		slow	3.2	1.6
calf-feed	1.2		1.5	1.5
5 % model	5.0		4.9	4.8
bentokarb	24.9		25.0	25.8

Identical results were obtained when investigating urebetin, bentokarb, cattle concentrates and szemakarb preparations, whether using standard or the two types of thermometric methods. Urevitid is a powder which wetted at a slow rate, consequently in its case when solid loading is applied the time/temperature curve can not be used for evaluation. However when it is measured in its solution twice the standard value is obtained due to by-reactions, thus in its case a calibration curve has to be prepared.

The last three samples were made of the stock solution prepared according to the standard simultaneously, and the results were very close.

It is to be remarked, that because of the large endotherm solution heat of urea, in case of higher urea content simple solution heat measuring technic also gives useful results.

When the standard method is used 8 chemicals, several types of glass utensils and 50-60 minutes are required to prepare spectrophotometric investigations. The permitted difference between parallel measurements is 5%.

In the case of thermometric measurements from solution are consequently 29, 30, 30 scale units; the average: 29.7, from which the individual results differ only in 1-2 %.

When solid samples with similar urea content were investigated the obtained results were 0.21, 0.19, 0.20 scale units an average of 0.20 units/mg, that is 5 % of differences between the individual measurements.

The time needed for the determination in the case of the base solution method was about 15, with solid samples 3 minutes.

Because of the small amounts of chemicals needed and the short time required by the thermometric method and simplicity of its use its application is recommended for fast industrial control.

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