



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/SE84/00274 (22) International Filing Date: 10 August 1984 (10.08.84) (31) Priority Application Number: 8304474.3 (32) Priority Date: 17 August 1983 (17.08.83) (33) Priority Country: SE</p> <p>(71) Applicant (for all designated States except US): ALFA-LAVAL AGRI INTERNATIONAL AB [SE/SE]; Box 500, S-147 00 Tumba (SE).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only) : NYLANDER, Claes [SE/SE]; Götgatan 70, S-582 31 Linköping (SE). ARMGARTH, Mårten [SE/SE]; Drottninggatan 41, S-582 27 Linköping (SE). LUNDSTRÖM, Ingemar [SE/SE]; Färgaregatan 10, S-582 52 Linköping (SE).</p>		<p>(74) Agent: CLIVEMO, Ingemar; Alfa-Laval AB, Box 500, S-147 00 Tumba (SE).</p> <p>(81) Designated States: AT (European patent), AU, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), NL (European patent), SU, US.</p> <p>Published With international search report. In English translation (filed in Swedish).</p>
<p>(54) Title: A METHOD AND A DEVICE FOR THE QUANTITATIVE ASSAY OF NH₃ IN A SAMPLE</p>		
<p>(57) Abstract</p>		
<p>The NH₃-concentration in a sample is determined by the aid of a device, comprising a layer of a polymer, based upon pyrrole or a derivative of pyrrole, or a derivative of such a polymer. The layer is acted upon by NH₃, originating from the sample, and its resistance is measured before and after this action. Increasing concentrations of NH₃ mean increasing resistance in said layer.</p>		

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A method and a device for the quantitative assay
of NH₃ in a sample.

This invention relates to a method and a device for the assay of
5 NH₃ in a sample. Primarily agricultural samples like manure
and barn air etc. are concerned.

A number of more or less sophisticated methods for the quantita-
tive assay of NH₃ in different types of samples have been sug-
10 gested and applied. Thus there are electrodes for the determina-
tion of NH₃/NH₄⁺. By adding alkali the equilibrium is dis-
placed towards NH₃. The method is primarily intended for labo-
ratories and demands relatively advanced instrumental equipment
and a sensitive electrode. Thus the method is relatively expen-
15 sive.

According to another laboratory method the sample is alkalized
and NH₃ is driven off, and captured in a vessel with acid. The
ammonia content is determined by titration. This method is in-
20 tended for laboratories only and demands skilled staff.

According to one further laboratory method a colour reaction
with Nessler's reagent is utilized, the intensity of a yellow
colour obtained being spectrophotometrically determined.
25

Straight chemical methods are also employed, e.g. by oxidizing
NH₃ to N₂ and measuring the change of volume or pressure
obtained.

30 None of these methods meets the demands of being simple, reli-
able, inexpensive and giving sufficient accuracy of measurement.
These demands are actual in many situations, for instance among
farmers for samples of manure, barn air etc.

35 The object of the present invention is to provide a method and a



device for the quantitative assay of NH_3 in a sample, especially manure and the like, the demands just mentioned being met.

5 According to the invention such a method is characterized in that the sample is brought into contact with a sensing body, comprising a polymer, either based upon pyrrole or a derivative of such a polymer, in such a way, that the NH_3 of the sample is caused to act upon the sensing body, the resistance of same
10 being determined before and after said action.

It has namely become obvious that the resistance of a polymer layer of the type just mentioned increases with rising NH_3 -concentration in a sample that is brought into contact with said
15 layer. Either the sample can be brought into direct contact with the layer, or gas phase, originating from the sample can be brought into contact with the layer. As liquid water disturbs the measurement it may be suitable to provide a membrane that is permeable for a gas but not for a liquid, between the sample and
20 said layer. This membrane may be somewhat spaced from the layer or be applied in direct contact with the polymer layer.

Considering the fact that a liquid like water disturbs the measurement it can be suitable to maintain the layer at a somewhat
25 higher temperature than the sample, e.g. 10° higher, so that condensate is avoided.

The invention shall now be described more in detail, reference being made to the accompanying figures, in which
30

figure 1 schematically shows a device according to the invention, and

figure 2 shows the resistance of a sensing layer as a function
35 of the time at different NH_3 concentrations.



In figure 1 a carrier plate of non conductive material is given number 1. On same there is applied a thin layer of polypyrrole 2, in contact with two leads 3,4, which are connected to a resistance meter 5, which is not further described. On the back side of the carrier plate there is glued a little circuit of resistor wire, which is not shown in the figure. This resistor wire is connected to a low voltage source. The carrier plate is fastened to a plug 6, which fits a cover to a test tube 7. In the figure this test tube is shown filled to about 1/3 with a sample 8.

In figure 2 there is shown the result of measurements of three test solutions of water, containing 500-1000-1500 ppm NH_3 , and a manure sample. When measuring, at a temperature of 20° in the samples and 30°C in the polymer layer, a 4 ml sample was introduced into the test tube, and 0.1 ml 10 M NaOH was added, whereupon the measuring device was inserted quickly into the test tube 7, which was then closed by the plug 6. By the addition of NaOH NH_4^+ and NH_3 in the sample were transferred to the gas phase. The resistance was determined continuously during 10 minutes and the curves in figure 2 were drawn. With the aid of the calibration curves it can be established that the NH_3 -concentration in the manure sample is about 750 ppm.



Claims

1. A method for the quantitative assay of NH_3 in a sample
c h a r a c t e r i z e d i n that the sample is brought
5 into contact with a sensing body, comprising a polymer, either
based upon pyrrole or a derivative of pyrrole, or a derivative
of such a polymer, so that the NH_3 of the sample is caused to
act upon the sensing body, the resistance of same being deter-
mined before and after said action.
- 10 2. A method according to claim 1, c h a r a c t e r i z e d
i n that the sample is brought into direct contact with said
sensing body.
- 15 3. A method according to claim 1, c h a r a c t e r i z e d
i n that the sample is brought into contact with the sensing
body.
- 20 4. A method according to claim 3, c h a r a c t e r i z e d
i n that said gas phase is brought into contact with the sen-
sing body after having passed a membrane, which is permeable for
a gas but not for a liquid.
- 25 5. A method according to any of claims 1-4, c h a r a c -
t e r i z e d i n that the sensing body is heated to a tem-
perature somewhat higher than the temperature of the sample in
order to avoid condensate on same when measuring.
- 30 6. A device for carrying out the method according to any of
claims 1-5, c h a r a c t e r i z e d by a sensing body,
comprising a polymer, either based upon pyrrole or a derivative
of pyrrole, or a derivative of such a polymer, connected by
leads to a resistance meter.



7. A device according to claim 6, characterized in that the sensing body comprises a carrier, onto which there is applied a relatively thin layer of said polymer.
- 5 8. A device according to claim 6, in which gas phase, originating from the sample, is brought into contact with the sensing body, characterized in that a membrane, permeable for a gas, but not for a liquid, is provided between the sample and the sensing body.
- 10 9. A device according to claim 8, characterized in that the membrane is made from polytetrafluorethylene.
- 15 10. A device according to any of claims 6-9, characterized in that the sensing body is provided with a circuit for electrical heating.



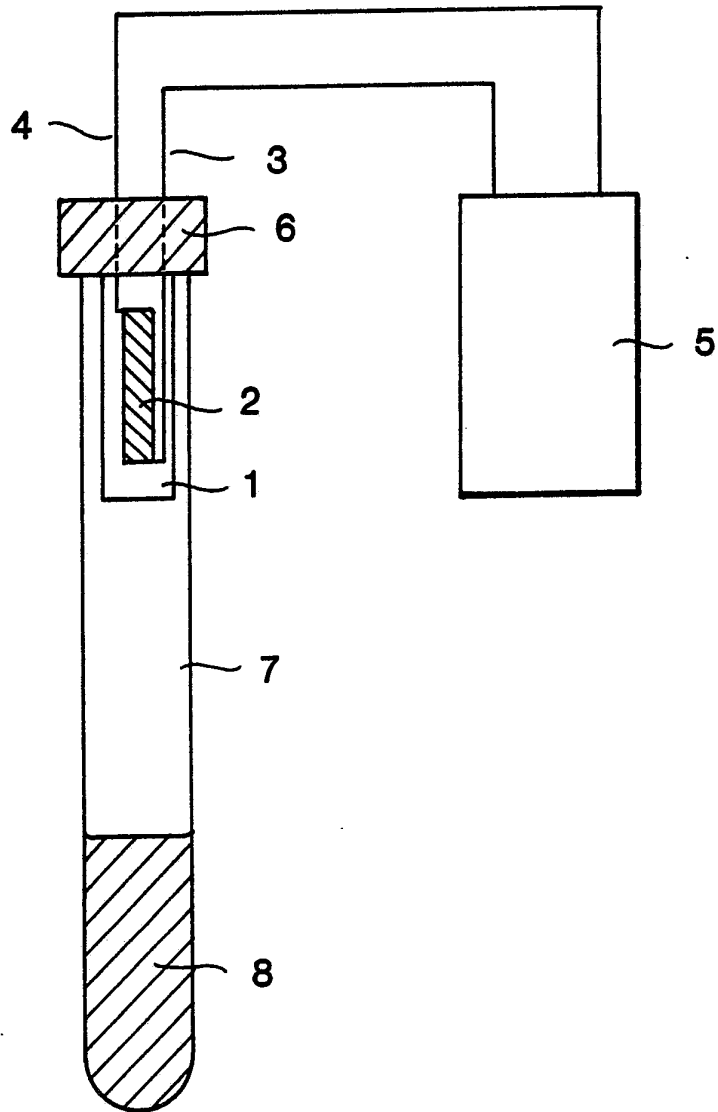


Fig. 1



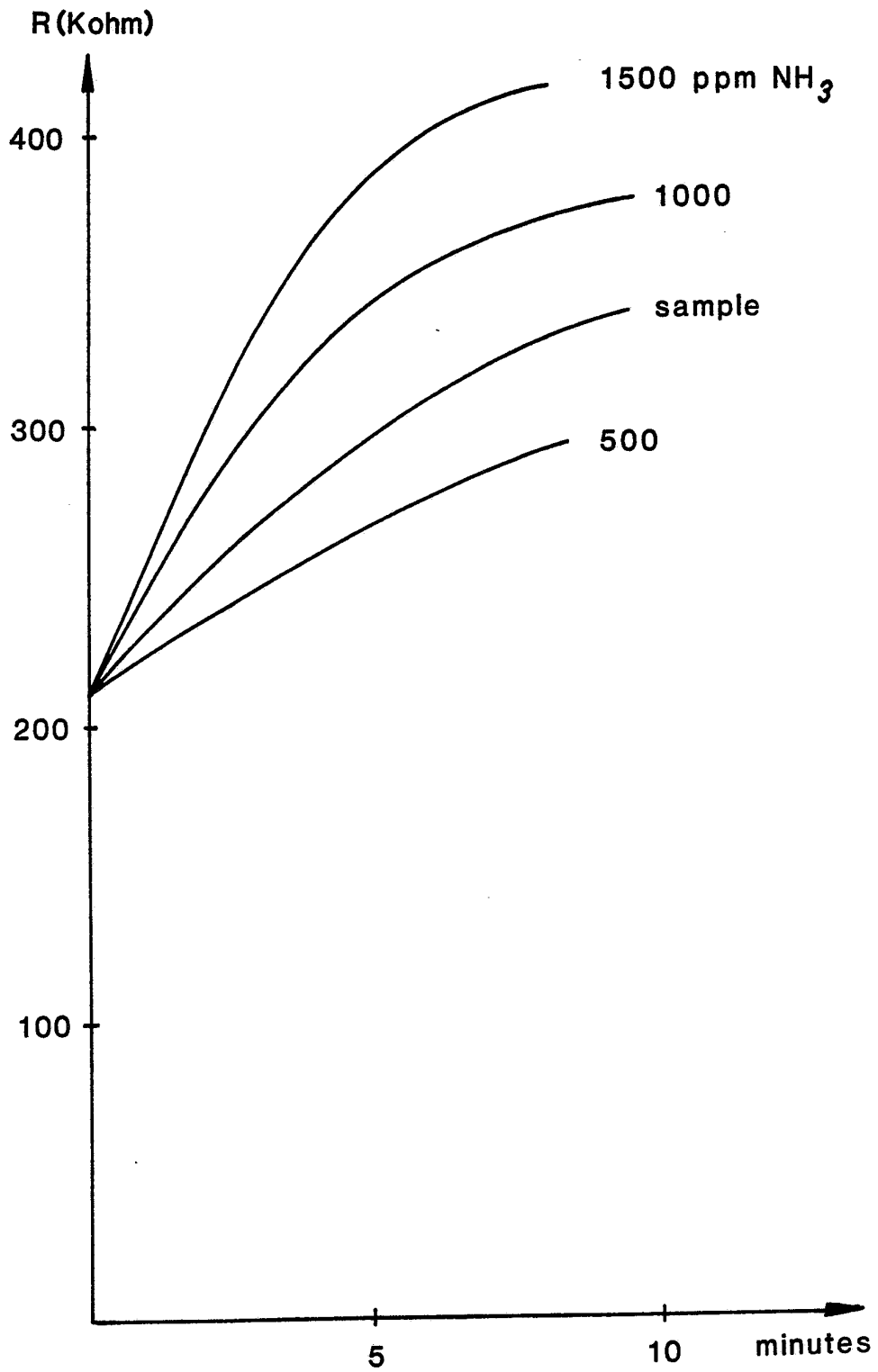
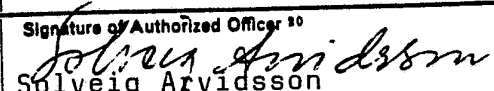


Fig. 2



INTERNATIONAL SEARCH REPORT

International Application No PCT/SE84/00274

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC 3 G 01 N 27/12		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
IPC 3 US C1	G 01 N 27/12, 31/06 <u>73:26</u> , 27R, 23; <u>324:65R</u>	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
SE, NO, DK, FI classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁶	Citation of Document, ¹⁶ with Indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
P	Chemical Abstracts, Vol 100 (1984) abstract nr 144174, Anal. Chem. Symp ser. 1983 17 (chem sens.) 203-7 (Eng), 30 April 1984	1-10
A	GB, A, 2 077 437 (EMI LIMITED) 16 December 1981	1-10
<p>⁹ Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ¹	
1984-10-24	1984 -10- 26	
International Searching Authority ¹	Signature of Authorized Officer ¹⁰	
Swedish Patent Office	 Solveig Arvidsson	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET**V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰**

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers 1, 6, because they relate to subject matter¹² not required to be searched by this Authority, namely:

These claims are unclear because of the sentence
"or derivate of such a polymer".

2. Claim numbers, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹³, specifically:

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.