

## **Qualitative and quantitative determination of trace amounts of aliphatic and aromatic amides and separation from ammonium impurities by molecular emission cavity analysis (MECA)**

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### **ABSTRACT**

Aliphatic amides (formamide 99.5%, and acetamide 97%) and an aromatic amide (benzamide 98.5%) were determined qualitatively and quantitatively at trace levels based on acid hydrolysis. Ammonia gas was detected by measuring the white band emission using thermal chemiluminescence in a cool hydrogen diffusion flame. Amides were determined quantitatively by hydrolysis with potassium hydroxide. Separation and identification of ammonium nitrogen present as impurities in amide were also studied.

### **INTRODUCTION**

Amide can be hydrolysed by alkali into the corresponding acid salt and ammonia gas, or by strong acids, e.g.  $H_2SO_4$  into the corresponding acid and inorganic ammonium salt. From these reactions, amides were identified chromatographically by boiling 0.2 g of the amide with 5 ml of 10% aqueous NaOH for three min, and testing the ammonia liberated using moist red litmus paper, or absorbing it in neutral copper(II) sulphate solution (Raymond 1973). This paper deals with the use of the white band emission of ammonia gas centered at 500 nm based on previous work (Belcher *et al.* 1977, 1981) with the additional improvements in sensitivity of at least 1000 times (Shakir 1990), ability of wavelength scanning, and an electronic output filter rise time of 0.2 msec–2 sec (Shakir 1988). This was used in several applications such as the determination of total nitrogen in soil (Shakir *et al.* 1988a), determination of ammonia gas in air and ammonium ion in artesian well waters (Shakir *et al.* 1988b) and the determination of total nitrogen in tobacco leaves using  $TiO_2$  and  $CuSO_4$  as catalyst (Shakir & Kadhir 1989). In order to study the determination of aliphatic and aromatic amides, the principle involved was to hydrolyse the amide in the reaction cell in a MECA (molecular emission cavity analysis) instrument (Shakir 1988), absorb the ammonia released in acid solution (6M  $H_2SO_4$ ), and subject the absorption solution to MECA using small hydrogen flame diluted with nitrogen, employing air as carrier gas to enhance the emission of ammonia.

## EXPERIMENTAL

### MATERIALS

Formamide 99.5%, acetamide 97%, and benzamide 98.5%. Analytical reagent grade of KOH,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

### EQUIPMENT

MECA instrument (Shakir 1988), hydrolysis and absorption vessels, and thermo-couple (iron-constantan).

### METHODOLOGY

#### *Wavelength scanning of formamide vapour in gaseous phase using MECA*

The reaction cell in MECA instrument was used to accommodate 2 ml of formamide, and wavelength scanning from 200–700 nm was carried out at  $\text{H}_2 : \text{N}_2$  of 1.75 : 1.25  $\text{l.min}^{-1}$ , using air as a carrier at 18  $\text{ml.min}^{-1}$  with a grating monochromator of 1200  $\text{nm.mm}^{-1}$  at inlet slit of 10 nm (or 20 nm), with electronic output filter rise time of 2 sec. The reaction cell was set at different temperatures to release the amide vapour and transfer it to the detector (i.e. cavity located in  $\text{H}_2\text{--N}_2$  flame). The emission profile of the blank (i.e. flame only, with the carrier gas passing through the empty reaction cell) gives the characteristic OH-free radical band centered at 306 nm. When placing concentrated ammonium solution in the reaction cell at the laboratory temperature of 13°C, the emission profile gave two bands; one centered at 306 nm, and the second (white) band centered at 500 nm for ammonia gas, which is thermally liberated, and gave a chemiluminescent emission in the flame. Repeating the same experiment but using concentrated formamide solution (density 1.1334  $\text{g.ml}^{-1}$ ), gave a clear OH band and another structureless weak band centered at 500 nm. This second band increased in intensity as more vapour was sent to the detector point (i.e. at a higher temperature in the reaction cell). This second band resembles the ammonia gas band, with the same maxima. All these profiles are shown in Fig. 1. The resemblance might be due to the thermal breakdown of the amide in the vapour phase, i.e. giving  $\text{NH}_2$  radicals and/or an NO—O continuum extending from 330–700 nm with a maximum around 500 nm. Two different temperatures were used, 250°C and 331°C, to generate a continuous feed of formamide vapour, which boils at 111°C. Repeating the same scanning experiment for acetamide and benzamide required higher temperatures for the amides to form their vapours (they boil at 221°C and 290°C, respectively). A condensation problem was met in the tube leading to the detector, and a higher temperature was not possible as the reaction cell could not stand a sudden rise from laboratory temperature (13°C) to above 300°C. To our knowledge the spectrum of formamide vapour is studied for the first time.

#### *Completeness of amide hydrolysis using potassium hydroxide*

During alkaline hydrolysis of amide, an absorption solution of 6M  $\text{H}_2\text{SO}_4$  was used in three successive absorption vessels of 100 ml capacity containing 60, 60 and 30 ml of 6M  $\text{H}_2\text{SO}_4$  followed by a guard tube containing neutral  $\text{CuSO}_4$  solution to

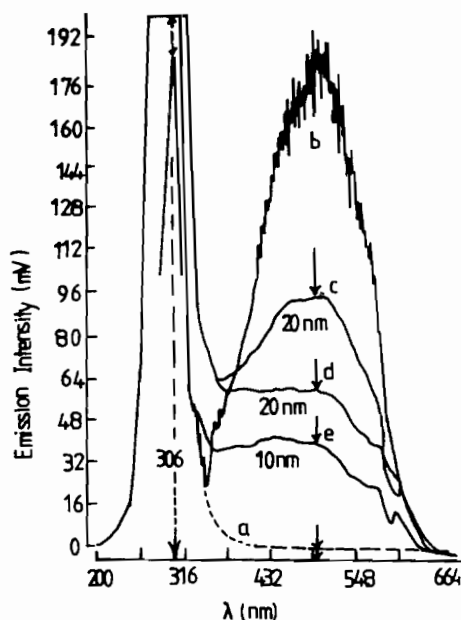


Fig. 1. Spectrum of (a)  $\text{H}_2\text{-N}_2$  flame, (b) ammonia vapour, and (c, d & e) formamide vapour using different inlet slit (10 and 20 nm); d, e at  $250^\circ\text{C}$  and c at  $331^\circ\text{C}$  block temperature.

observe any escaped ammonia gas. The 150 ml of 6M  $\text{H}_2\text{SO}_4$  solution were collected to 500 ml in a volumetric flask to give a final acid molarity of 1.8 M  $\text{H}_2\text{SO}_4$ . One ml of this solution was subjected to MECA analysis at a heating block surface temperature of  $175^\circ\text{C}$  coupled with a time switch adjusted to 50%. Fig. 2 shows three plots of temperature measurements of the reaction block (Fig. 2a), 1 ml of absorption solution when KOH was added (Fig. 2b), and 1 ml of absorption solution (when KOH was added) in the reaction block (Fig. 2c). In the last case, temperature rose to  $65^\circ\text{C}$  during the time required for complete release of ammonia gas from absorption solution. When a larger amount of KOH is used, less time is needed for each single measurement due to increased rate of reaction (high alkalinity, heat of neutralisation, and heat of solution of solid KOH pellets in 1.8 M  $\text{H}_2\text{SO}_4$ ). Fig. 3a shows that higher sensitivity can be obtained. For continuous measurement it was noted that 4 pellets of KOH were more convenient. To test if any amide remained unhydrolysed in the round bottom flask used for hydrolysis, the solution in the flask was subjected to MECA. No released ammonia or amide (Fig. 3b) were detected.

#### Acid hydrolysis of amides

To 0.5 g of the amide (formamide, acetamide or benzamide) was added 1 ml of conc.  $\text{H}_2\text{SO}_4$  (36 M) and the mixture refluxed for 3 min in a 10 ml round bottom flask. The solution in the flask was completed to 20 ml to have a final concentration of 1.8 M  $\text{H}_2\text{SO}_4$ . One ml of the resulting solution was subjected to MECA. Fig. 4A shows a sample of these measurements. Two peaks can be seen; the first appears quickly and might be due to ammonium ion either already present in the amide

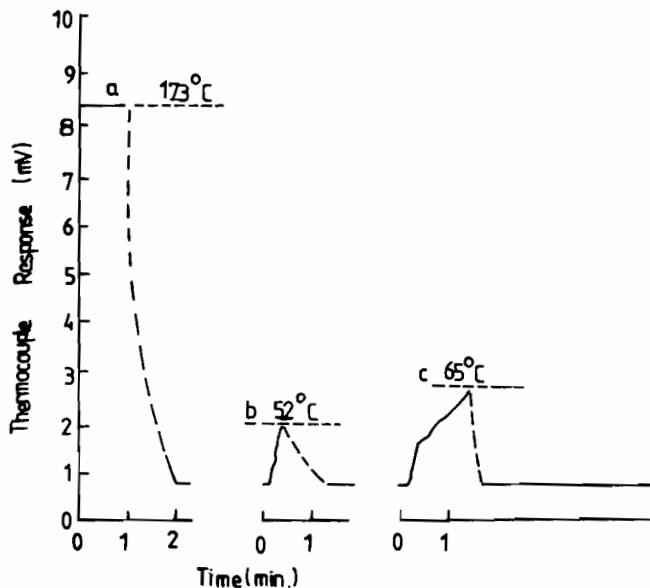


Fig. 2. Temperature-time course of (a) the reaction block, (b) 1 ml of the absorption solution when KOH was added, and (c) 1 ml of the absorption solution placed in the reaction block (normal working procedure).

solution as impurity or formed as a result of hydrolysis, while benzamide shows that it is hardly attacked under the experimental conditions described above. Therefore acid hydrolysis of this amount of reactant was rejected. Using a larger amount of reactant, condensation of solid is noticed on the condenser wall. When the reaction

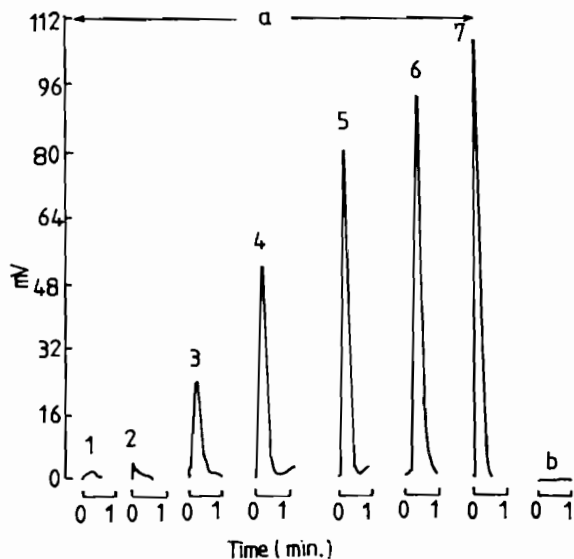


Fig. 3. Variation of emission intensity with time showing (a) the effect of the amount of KOH used to release the ammonia gas from an absorption medium of 1.8 M  $H_2SO_4$  (numbers above peaks indicate the number of KOH pellets), and (b) response from 1 ml of the hydrolysed medium (no KOH added).

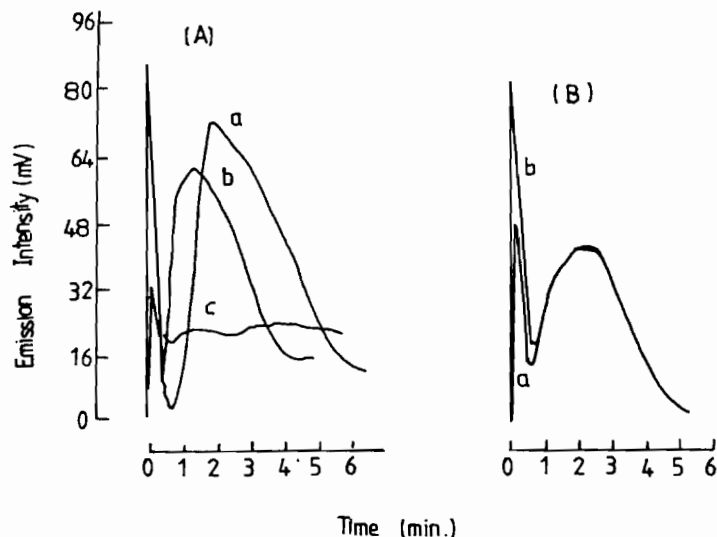


Fig. 4. Emission-time profile of (A) acid-hydrolysed amides: (a) formamide, (b) acetamide, and (c) benzamide; (B) 13.25 mg of solid acetamide (a), and 13.25 mg of solid acetamide + 1 ml of 500 ppm  $\text{NH}_4^+$  as  $(\text{NH}_4)_2\text{SO}_4$  (b).

proceeded for a longer period of time, a solid residue remained at the bottom of the flask due to precipitation of insoluble benzoic acid, so another step is added in that the solution must be filtered. Up to 1 : 1 mole ratio was tried and two peaks always appeared. To prove that the first peak is due to ammonium ion, e.g. from ammonium formate, ammonium acetate or ammonium benzoate, 1 ml of 500 ppm  $\text{NH}_4^+$  as  $(\text{NH}_4)_2\text{SO}_4$  was added to 0.01325 g of solid acetamide and subjected to MECA. It showed an increase in the first peak compared to the same weight of acetamide when 1 ml of distilled water was used instead of 1 ml of ammonium ion solution (Fig. 4B). No change occurred in the second peak profile within the reproducibility of the measurements.

#### Alkaline hydrolysis of amides

Formamide, acetamide or benzamide (0.5 g) was placed in a round bottom flask (10 ml capacity fitted with inlet for  $\text{N}_2$  gas as a carrier and reflux condenser), followed by the addition of 0.64946 g KOH and heated to  $50^\circ\text{C}$  for 3 min. The gas released was transferred with the aid of  $\text{N}_2$  gas at 60 bubbles/min to three successive absorption vessels connected in series containing 60, 60, and 30 ml of 6M  $\text{H}_2\text{SO}_4$ . The third absorption vessel was connected to a guard tube containing neutral copper sulphate solution (4 M). The solution in each absorption flask was collected and completed to 500 ml in a volumetric flask to give a final concentration of 1.8 M with respect to  $\text{H}_2\text{SO}_4$ . When 1 ml of this solution was subjected to MECA, it gave a single symmetric peak (Fig. 5) for each of the three amides. Using larger molar ratio of reactant and higher temperatures, some of the amide escaped to the first absorption flask and this was detected when the first absorption solution was subjected to MECA (i.e. two peaks). On this basis a calibration graph was constructed

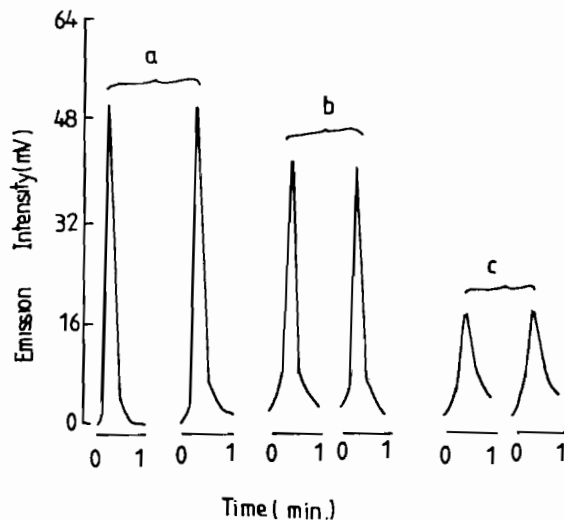


Fig. 5. Emission intensity *v.* time of 1 ml of hydrolysed amide (repeated twice) using KOH: (a) formamide, (b) acetamide, and (c) benzamide.

using  $(\text{NH}_4)_2\text{SO}_4$ . Solutions containing 0.0, 50, 100, 150, 200, 250, 300, 350, 400, 450, and 500 ppm  $\text{NH}_4^+$  as  $(\text{NH}_4)_2\text{SO}_4$  in 1.8 M  $\text{H}_2\text{SO}_4$  were prepared. A linear calibration graph corresponding to:

$$\text{Emission intensity (mV)} = 0.14 (\text{concentration ppm } \text{NH}_4^+) + 0.58$$

was obtained. When the hydrolysed amide was subjected to MECA through the absorption solution of each amide, it gave 350, 293, and 132 ppm  $\text{NH}_4^+$  (average of six successive measurements on the same solution) for formamide, acetamide, and benzamide respectively. The results obtained are shown in Table 1.

#### *Direct determination of amide (formamide, acetamide, and benzamide)*

The use of solid or liquid amides directly (no treatment) using the parameters fixed in the previous sections, gave two separate peaks; each measurement lasted 7–8 min. The first peak is due to ammonium ion, while the second peak, which generated slowly, is due to ammonia from amide hydrolysis. Fig. 6 shows the result of a preliminary investigation of the possibility of direct determination of amides, while Fig. 7 exhibits the qualitative profile of different weights (1.71–5.70 mg) of acetamide analysed as mentioned above. The method is not so suitable as the determination using alkaline hydrolysis, since it is difficult to weigh the same amount each time.

Table 1. Determination of amides

Amide (0.5 g)	Theoretical ( $\text{NH}_3$ ) g	Practical ( $\text{NH}_3$ ) g	Recovery %
Formamide	0.188	0.165	87.8
Acetamide	0.144	0.138	95.8
Benzamide	0.070	0.062	88.6

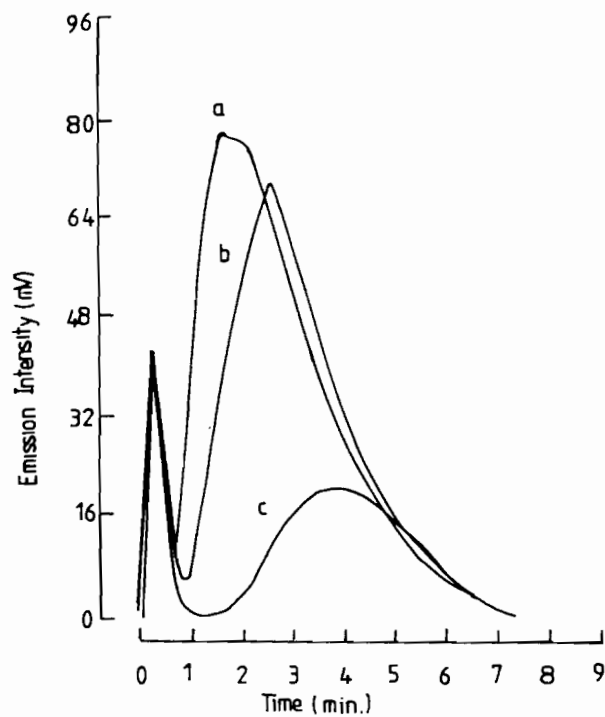


Fig. 6. Preliminary investigation of emission-time profile of solid amides: (a) formamide, (b) acetamide, and (c) benzamide.

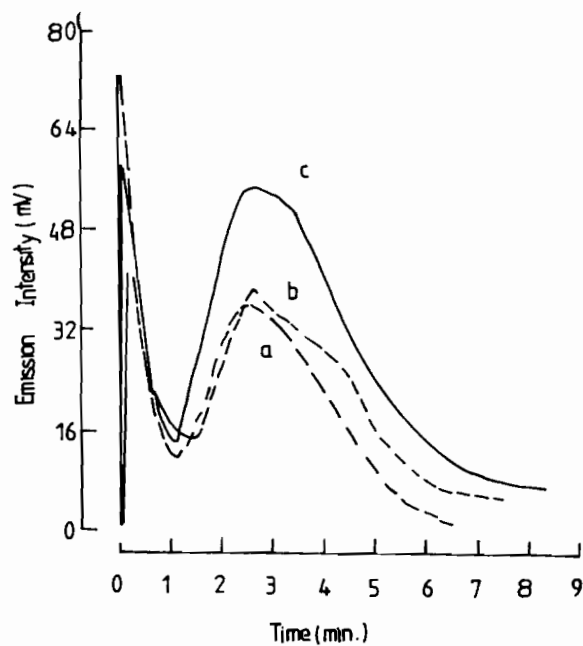


Fig. 7. Emission-time profile of solid acetamide: (a) 1.71 mg, (b) 2.10 mg, and (c) 5.7 mg.

*Proof of the existence of two forms of nitrogen*

On the basis of the above experiments, two peaks were observed: a sharp one due to ammonium nitrogen and a second due to hydrolysis of the amide. For further proof of the existence of two identifiable peaks from the amide, a blank was run in which distilled water and 0.37112 g KOH (with no acetamide) were used. It gave no emission. This treated water was used for further study of amides, and gave two peaks. This indicates that two forms of nitrogen are present. Also the first peak has less height, most probably due to losses of ammonium because of the treatment of water with alkali before insertion into the instrument. This experiment proves that this method can be used for the separation of ammonium and amide.

## DISCUSSION

Formamide, acetamide, and benzamide can be determined quantitatively using alkaline hydrolysis, where both ammoniacal and amide nitrogen can be converted into one single form, i.e. ammonia. From all the experiments conducted in this work, two peaks were obtained, which were both identified as ammoniacal or amide nitrogen. Acid hydrolysis of the amide was avoided mainly because of volatilization of the acid resulting from the amide. Direct determination with no pretreatment cannot be used for quantitative analysis but can be used selectively for qualitative analysis. This study offers a means of separation, identification, and determination of amides.

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## التقدير النوعي والكمي للكميات الضئيلة من الأمايد الأليفاتية والأروماتية وفصلها من شوائب الأمونيوم بتحليل الإنبعاث الجزئي

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### خلاصة

تم تقدير كميات ضئيلة من الأمايد الأليفاتية (الفورماميد والأستياميد) والأمايد الأروماتية (البنزاميد) نوعيا وكميا بعد تحليلها تحليلا مائيا باستخدام حامض أو قلوي قوي . وتم الكشف عن غاز الأمونيا عن طريق قياس الحزمة الطيفية المتولدة منه بفعل التآلق الكيماوي في هبة هيدروجين تنافضية . كما تم تقدير الأمايد بشكل كمي باستخدام قلوي قوي (هيدروكسيد البوتاسيوم) . وتمت دراسة فصل وتشخيص شوائب الأمونيوم الموجودة في الأمايد .

