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RESEARCH ESTABLISHMENT

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ABSTRACT

Ammonium uranate (AU) powders were precipitated from a uranyl nitrate solution using gaseous ammonia to determine the effect of pH of precipitation on their composition and morphology. Increasing pH of precipitation increased the ammonia and nitrate contents and the specific surface area but decreased the crystallite size of the AU powders. The specific surface area was also increased by increasing the ammonia content of the powder. The composition and morphology of the powders were similar to those reported in the literature for AU precipitated with NH_4OH.

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AMMONIA; AMMONIUM HYDROXIDES; AMMONIUM URANATES; CHEMICAL COMPOSITION; COMPARATIVE EVALUATIONS; GASES; MORPHOLOGICAL CHANGES; pH VALUE; POWDERS; PRECIPITATION; SURFACE PROPERTIES

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ENERGY DEPENDENCE; ENERGY SPECTRA; ERRORS; FUNCTIONS; ITERATIVE METHODS; LIMITING VALUES; MATRICES; NEUTRON SPECTRA; RESOLUTION; SPECTRA UNFOLDING; STATISTICS;

CONTENTS

1. INTRODUCTION

Uranium dioxide powder from which nuclear fuel pellets are produced is commonly prepared by heating ammonium uranate (AU) in hydrogen. In general, AU is precipitated commercially from a uranyl nitrate solution with aqueous ammonium hydroxide. A literature survey [Woolfrey 1968] showed that the AU powder characteristics (composition, surface area, particle size and density) are strongly dependent on the precipitation conditions (namely pH, uranium concentration, temperature, rate of precipitation and nature of the precipitant).

The first technology developed at Lucas Heights for the production of AU was based on precipitation with gaseous ammonia [Ramm & Quaass 1968]. Later, a large scale process using aqueous ammonium hydroxide was developed [Alfredson 1969; Janov *et al*. 1971; Alfredson 1972]. Gaseous ammonia was chosen initially because it appeared to offer advantages in controlling the precipitation process [Watson 1958] and was reported to produce a uniformly smaller particle size [Watson 1958; Galkin *et al*. 1966]. Little information was available in the literature about the products formed by continuous precipitation with gaseous ammonia [Woolfrey 1968]. Preliminary development results indicated that pH was the dominant factor affecting the AU powder characteristics, so its effect on the composition and morphology of the AU powder produced was investigated while all other variables were held constant.

2. EXPERIMENTAL

The AU precipitates were prepared by continuous precipitation from a 0.63 molar uranyl nitrate solution with gaseous ammonia at 42°C. The equipment and techniques used have been described elsewhere [Ramm & Quaass 1968]. The uranyl nitrate flow rate was kept constant (0.17 mol U min^{-1}) and the ammonia flow rate was progressively increased to raise the pH to the desired value (Figure 1). The pH was measured with an E.I.L. model 23A pH meter with automatic temperature compensation. The electrodes were washed with demineralised water every ten minutes during operation to minimise the buildup of precipitate on the electrode surface and prevent loss of sensitivity; they were also immersed in acid solution and recalibrated every fifteen minutes. Under these conditions, the pH could be measured with an accuracy of ± 0.1 (E. Ramm, private communication) and a stable pH could be maintained for the duration of the precipitation.

'Batches' of AU were precipitated at thirteen different levels of pH within the range 4.2 to 10. In a separate experiment, the ammonia content of an AU precipitated at pH 4.2 was further increased by standing the powder above ammonium hydroxide solution, or in gaseous ammonia, in a previously evacuated desiccator for 5 days at room temperature.

AU powders precipitated from a uranyl nitrate solution generally contain residual nitrate as a major impurity. The majority of the nitrate can be removed by washing the precipitate with either water or alcohol. However, washing with water also removes ammonia [Janov *et al.* 1971], most of which is associated with the nitrate removal, but some of the combined ammonia in the AU structure may also be removed by an exchange mechanism [Cordfunke 1962; Stuart & Whateley 1969]. Thus the amount of nitrate and, to some extent, ammonia present in an AU powder depends on the amount of washing the precipitate receives. For this reason, the washing technique was standardised for all precipitates. After washing twice in demineralised water, two alcohol washes were then used to try to remove as much nitrate as possible yet minimise the removal of combined ammonia from the AU structure. The washing and drying procedure for the precipitates has been described fully elsewhere [Woolfrey 1974] together with the techniques for measuring the specific surface area and X-ray crystallite size of the powders.

Where applicable, linear regression techniques were used to fit straight lines to the data. These are shown as continuous lines on the relevant figures whereas the 95 per cent confidence limits for the distribution of the data about the regression line are shown by broken lines. The relevant correlation coefficient (r) is quoted together with the probability (p) that such a correlation could result from purely random sampling of an uncorrelated population [Paradine & Rivett 1953].

3. RESULTS AND DISCUSSION

Figure 2 and Table 1 show that the pH of precipitation has a profound effect on both the composition and morphology of the AU powders produced.

3.1 Effect of pH of Precipitation on AU Composition

By analogy to the cation exchange results of Stuart & Whateley [1969], the precipitation of ammonium uranate may be represented by the equation:

$$UO_2^{++} + xNH_4^+ + 2H_2O \rightarrow UO_2(OH)_{2-x}(O^-NH_4^+)_x + (2 + x)H^+ \quad . \qquad (1)$$

One would expect that, even for non-equilibrium conditions, both pH and the NH_3 concentration would affect the AU composition. Since the pH of precipitation was increased by increasing the NH_3 feed rate (Section 2), it is not possible to assess the relative importance of these two parameters. The term pH is used in subsequent discussions to refer to the conditions in which both these parameters have been varied simultaneously (Figure 1).

Both the total and combined ammonia content of the powders generally increased with increasing pH of precipitation ($r = 0.63$, $p \sim 0.02$ and $r = 0.80$, $p \sim 0.001$ respectively (Figure 2)). The combined ammonia in the AU was calculated by subtracting the ammonia content associated with the nitrate, based on the assumption that the nitrate is present as stoichiometric NH_4NO_3. Washing reduced the nitrate content of the solids to a level below which it was extremely difficult to remove further nitrate (Figure 2). This implies that the residual nitrate is tightly bound to the surface or occluded within the solid. A statistical analysis of the data indicated that there was no significant correlation between nitrate content and pH ($r = 0.3$, $p > 0.1$) because of the large scatter in the nitrate data. The average NO_3/UO_3 content was ~ 0.06. Thus the reduced scatter observed in the combined ammonia - pH correlation is due to the absence of the ammonia associated with the variable nitrate content.

A similar trend of increasing ammonia content of AU with increasing pH has been reported by a number of investigators [Woolfrey 1968] for precipitation with an NH_4OH feed solution. A study of the adsorption equilibrium between $UO_2(OH)_2.H_2O$ and ammonium nitrate solution [Stuart & Whateley 1969] also showed increased ammonia adsorption from more concentrated solutions. As discussed previously, the postulated equilibrium precipitation conditions (Equation 1) indicate that the ammonia content of the AU would be expected to increase as the pH and/or ammonia concentration of the reaction increased.

Examination of Figure 2 shows an apparent correspondence between the trend in individual NH_3 and NO_3 data points suggesting a possible correlation between the two. This is shown in Figure 3 where residual nitrate content is seen to increase with increasing total NH_3 content of the AU powders ($r = 0.87$, $p < 0.001$). The slope (0.46) indicates that, after allowance for the minimum ammonia content, the total ammonia increases with residual nitrate in an approximate 2:1 ratio. Ainscough & Oldfield [1962] reported a similar correlation between total NH_3 and NO_3 contents for AU precipitated with NH_4OH; but the observed ratio was approximately 1:1, *i.e.* the AU had a fixed composition (combined NH_3 content) and all the excess ammonia could be attributed to NH_4NO_3.

There has been considerable argument concerning the nature of the AU precipitate. Cordfunke [1962,1970] reported the presence of four distinct compounds which he designated:

I = $UO_3 \cdot 2H_2O$,
II = $UO_3 \cdot 0.33NH_3 \cdot 1.67H_2O$,
III = $UO_3 \cdot 0.5NH_3 \cdot 1.5H_2O$, and
IV = $UO_3 \cdot 0.67NH_3 \cdot 1.33H_2O$,

with intermediate compositions representing two-phase mixtures. Debets & Loopstra [1963] showed that these compounds had distinctive X-ray diffraction patterns. Later results of Stuart & Whateley [1969] indicated that the AU system at equilibrium is continuous with no intermediate stoichiometric compounds. Price & Stuart [1973] concluded that the 'compounds' observed by Cordfunke are in fact metastable, chemically non-uniform products formed under non-equilibrium conditions. However, there is no doubt that changes in composition, even in the equilibrium product, induce detectable changes in the X-ray diffraction patterns [Stuart & Whateley 1969; Price & Stuart 1973].

The X-ray diffraction patterns of the AU powders were initially classified in terms of Cordfunke's compound nomenclature. The effect of pH of precipitation on the indexed compounds is shown in Table 1. The change in d-spacings of the three most intense peaks with combined ammonia content of the AU is shown in Figure 4. The scatter in results is caused by the effects of peak overlapping and crystallite size line broadening. However, a general and continuous trend of lattice contraction with increased ammonia content is evident. The roman numerals at the top and bottom of the figures indicate the type of compound reported in Table 1. The solid triangles with associated roman numerals are the d-spacings from the compounds reported by Debets & Loopstra [1963]. This continuous trend supports the conclusion of Price & Stuart [1973] that the AU system is continuously variable with no stoichiometric compounds present.

Although nitrate ions are present in quantities up to 3 wt.% of the AU, X-ray diffraction patterns showed no evidence of the presence of ammonium or uranium nitrate. However, the detection of ammonium nitrate in the AU would be difficult since reflections from the heavy uranium atoms dominate the X-ray powder diffraction patterns [Debets & Loopstra 1963]. In several cases, comparison between pairs of similar AU powders showed that an increase in nitrate content (∿ 0.05 in NO_3/UO_3) also produced a contraction (∿ 1.5 per cent) in the AU lattice when the combined ammonia content remained constant or even showed a small decrease. These limited results suggest that nitrate also may cause contraction of the AU lattice.

It has been proposed [Stuart & Whateley 1969; Price & Stuart 1973] that AU resembles lamellar clay minerals, consisting of lamellae formed by the uranium-oxygen lattice with coordinated molecular water, OH groups and $-ONH_4$ groups between these layers. The structural analyses of Christ & Clarke [1960] and Debets & Loopstra [1963] support such an interpretation. The change in the position of the X-ray diffraction peaks with NH_3 content observed in the present studies of AU further confirms this analogy, since the basal reflections observed from montmorillonite type minerals also vary in position, depending on the separation of the lamellar alumino-silicate layers which is controlled by the nature and amount of exchange cations present between these layers [MacEwan 1961]. Barrer & Meier [1958] have found that ammonium nitrate complexes can form inclusions in zeolites, owing to the open nature of the zeolitic structure, producing lattice distortion without the diffraction pattern of the original salt being observed. Although no directly comparable observations could be found in the literature for lamellar clay minerals, complexes with other inorganic molecules can be formed between the layers in montmorillonite type minerals [MacEwan 1961]. Similarly, the residual nitrate in AU powders may form ammonium nitrate complexes in the open structure of AU without the specific X-ray diffraction pattern from the nitrate complex being observed.

3.2 Effect of pH of Precipitation on AU Particle Morphology

Electron microscopy of alcohol-dispersed material showed that all the AU powders consisted of very thin plates of hexagonal or related shapes with a wide range of particle sizes (Figure 5). The powders precipitated at pH 4.2 and 4.6 contained a high proportion of large particles up to 2 μm in length, but in all other powders the largest particles measured approximately 0.1 μm. The average particle size generally appeared to decrease with increasing pH of precipitation and the particles became more equi-axed. Basically similar powder characteristics have been observed for AU precipitated with NH_4OH [Doi & Ito 1964; Janov *et al.* 1971].

The effect of pH of precipitation on the specific surface area and X-ray crystallite size of the AU powders is shown in Figure 2. The dependence of the surface area of the AU on pH is more complicated than is usually reported in the literature, but Jakes & Landspersky [1964] have observed similar curves for AU precipitated with NH_4OH. There is a general trend of an increase in surface area of the AU with increasing pH of precipitation. Several apparent maxima occur but the reasons for these are not evident. Jakes & Landspersky [1964] have attempted to explain their presence in terms of changes in the structure of the precipitate associated with changes in the observed compounds. Such an explanation is not tenable if the compounds are due only to non-equilibrium composition effects. Also, in the present results there is no correlation between the surface area maxima and/or minima and observed changes in the compounds present in the AU. The X-ray crystallite size shows a general tendency to decrease with increasing pH (Figure 2) with some variations which appear to be associated with variations observed in the trend of the surface area results.

The correlation between specific surface area and X-ray crystallite size is shown in Figure 6. The solid line represents the theoretical relationship for equi-sized, thin plates (observed by electron microscopy). This relationship is given by

$$s = f/(\rho t) \quad , \qquad (2)$$

where s is the specific surface area, f is a shape factor ($\sim$ 2 for equi-sized thin plates [Gregg & Sing 1964]), ρ is the density ($\sim$ 5 g cm^{-3} for AU [Clayton & Aronson 1961; Dembinski *et al.* 1966; Janov *et al.* 1971]) and t is the particle thickness. Because of the packing of such plates, the measured X-ray crystallite size will correspond to the plate thickness. The BET results are in relatively good agreement with the X-ray based predictions, suggesting that the particles which determine the measured BET surface area are thin, plate-like single crystals. Selected area electron diffraction indicated that the long plates with well developed crystallographic shapes were single crystals. Some of the smaller irregularly shaped plates were polycrystalline.

The pH of a solution has a profound effect on the particle size of a precipitate because it affects the relative rates of nucleation and growth of crystallites. The 'solubility' of AU decreases from approximately 10 g ℓ^{-1} at pH 4 to 10^{-14} g ℓ^{-1} at pH 9 [Stevenson 1964]. Thus as the pH increases, nucleation is increasingly favoured over crystallite growth, producing the observed trend of increasing surface area and decreasing crystallite size of the AU precipitate.

The specific surface area and crystallite size of the AU powders showed a significant correlation with the ammonia content of the AU (Figure 7). No significant correlation could be made with the nitrate content because of the large amount of scatter in the nitrate data. It is difficult to assess intuitively the physical significance of this correlation since both the composition and morphology of the powders are strongly dependent on the pH of precipitation.

To check the observed dependence on the NH_3/UO_3 ratio, the ammonia content of a nitrate-free AU was increased by placing it above a solution of NH_4OH or in a gaseous atmosphere of NH_3, as described in Section 2. When placed above the NH_4OH solution, the NH_3/UO_3 ratio increased from 0.37 to 0.54 and this produced a 100 per cent increase in the initial specific surface area and a decrease of 15 per cent in the X-ray crystallite size. This measured change in X-ray crystallite size is barely significant since the accuracy of the method is about ± 10 per cent.

To check if the water vapour content of the atmosphere was an important factor, dry ammonia gas was used and a similar increase in the ammonia content of the AU increased the specific surface area by 65 per cent. These results confirm that the surface area and X-ray crystallite size of the AU powders are related to composition. However, the observed change in X-ray crystallite size ($\sim$ 15 per cent) is much less than would be predicted from the precipitation data correlation for the corresponding change in surface area ($\sim$ 100 per cent).

The structure of AU consists of hexagonal or pseudo-hexagonal layers of composition $UO_2(O_2)_\infty$, with the O and N atoms of water and ammonia situated between these layers [Debets & Loopstra 1963]. The observed increase in surface area during these latter experiments is possibly due to the adsorption of extra ammonia by the structure; this produces intra-layer separation which then becomes accessible to the nitrogen molecules used in the BET surface area measurement. This would also explain why the large change in the observed specific surface area is associated only with a minor change in the X-ray crystallite size. The correlation between ammonia content and surface area/X-ray crystallite size observed during precipitation would appear, therefore, to result from the precipitation conditions simultaneously controlling both the amount of ammonia adsorbed and morphology of the precipitate.

4. COMPARISON OF NH_3 AND NH_4OH PRECIPITANTS

It is difficult to assess the relative effects of using gaseous NH_3 or aqueous NH_4OH as the precipitant since the precipitation of ammonium uranate occurs by heterogeneous nucleation and the design of the apparatus has a major influence. Because of the pressure of developmental work, no comparative precipitations could be carried out in the same equipment. However, from the comparisons made during the discussion of the results (Section 3) it is obvious that the composition and morphology of the AU is similar whichever of the two precipitants is used. Comparison of the surface areas shown in Figure 2 with those reported for precipitation with NH_4OH over a similar range of pH [Jakes & Landspersky 1964; Janov *et al.* 1971] does not substantiate the claim by Watson [1958] and Galkin *et al.* [1966] that finer powders are produced. Thus, the only advantage of using gaseous ammonia over NH_4OH would appear to be in the relative ease of control of the precipitation process [Watson 1958; Ramm & Quaass 1968].

5. CONCLUSIONS

The results showed that increasing the pH of precipitation increased the ammonia and nitrate contents and, the specific surface area, and decreased the crystallite size of AU powders precipitated with gaseous NH_3. The specific surface area was also increased by increasing the ammonia content of the powder. The composition and morphology of these powders were similar to those reported in the literature for AU precipitated with NH_4OH.

6. ACKNOWLEDGEMENTS

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TABLE 1

EFFECT OF pH OF PRECIPITATION ON THE TYPE OF AU FORMED

pH	AU Type*			
	I	II	III	IV
4.2		M	VMi	
4.6		M	VMi	
5.0		M	VMi	
5.9		M	VMi	
6.4		M	M	
6.9		M	M	M
7.1		Mi	M	M
8.0		Mi	M	M
8.6		Mi	M	M
9.1			M	M
9.4			M	M
10.0			M	M

*Cordfunke's [1962] AU compound nomenclature is used

M = major, Mi = minor,

VMi = very minor

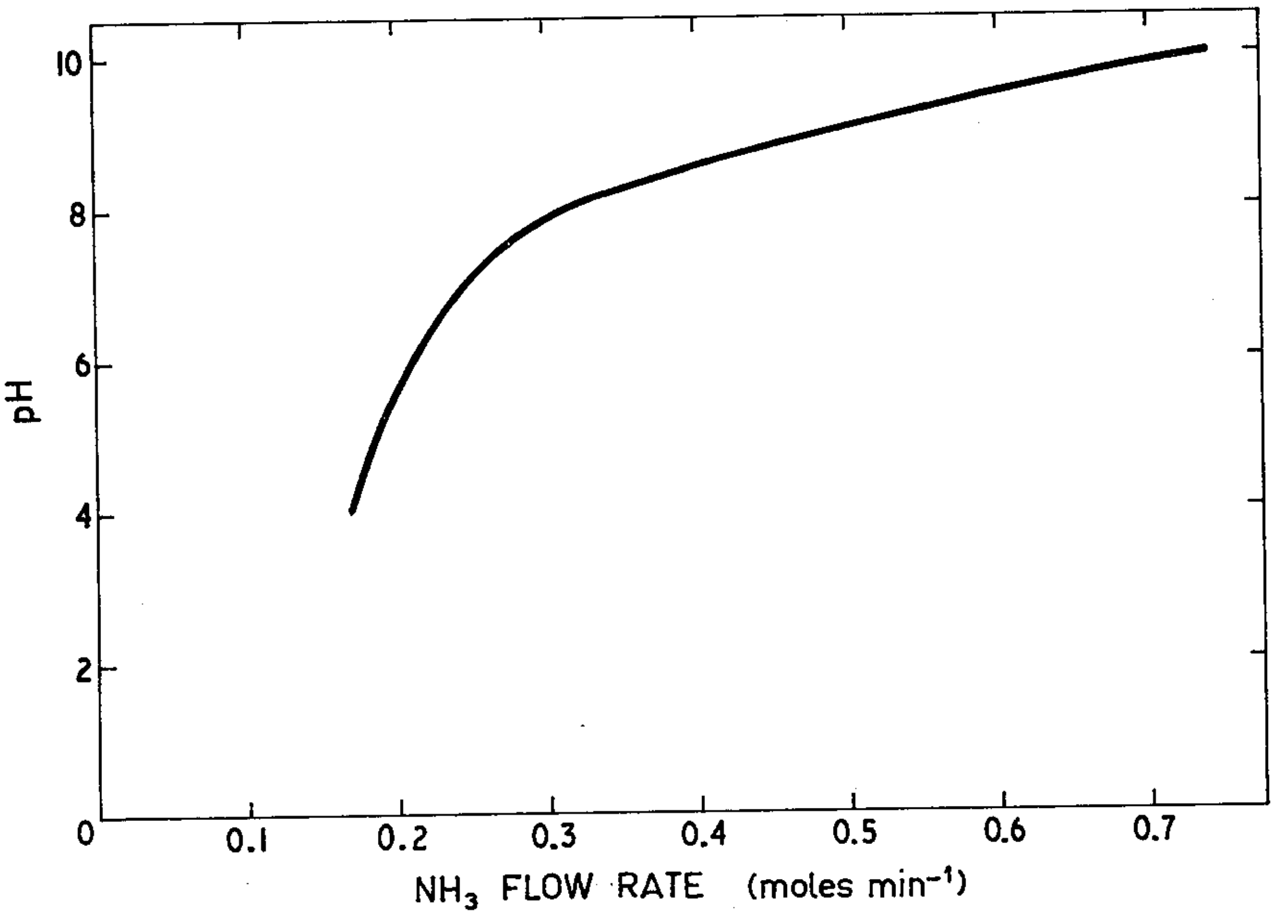


FIGURE 1. RELATIONSHIP BETWEEN pH AND AMMONIA FLOW RATE DURING THE CONTINUOUS PRECIPITATION OF AU WITH GASEOUS AMMONIA

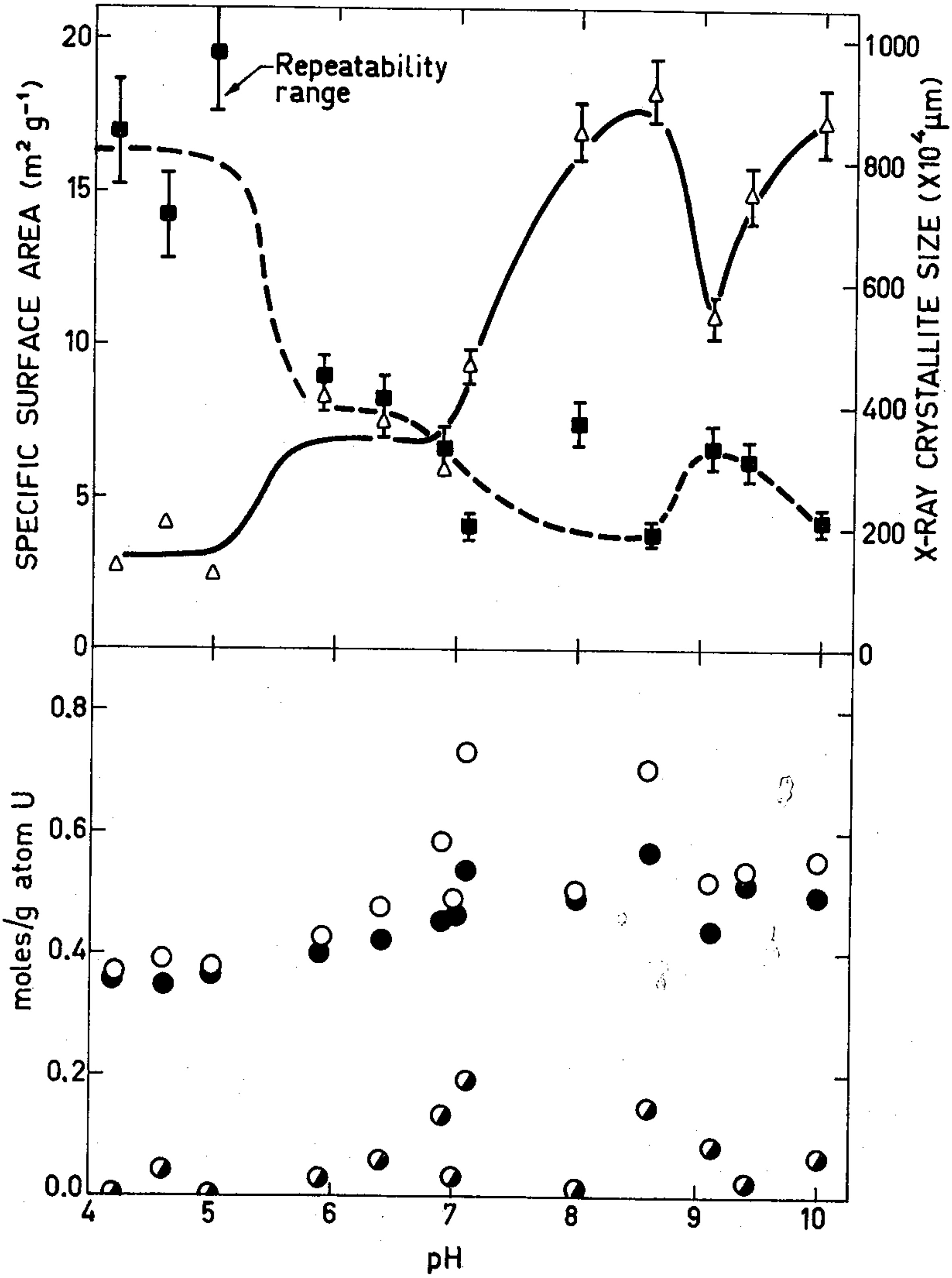


FIGURE 2. EFFECT OF pH OF PRECIPITATION ON THE COMPOSITION (O total ammonia, ● combined ammonia, ◐ nitrate content) AND MORPHOLOGY (Δ specific surface area, ■ x-ray crystallite size) OF THE AU POWDERS

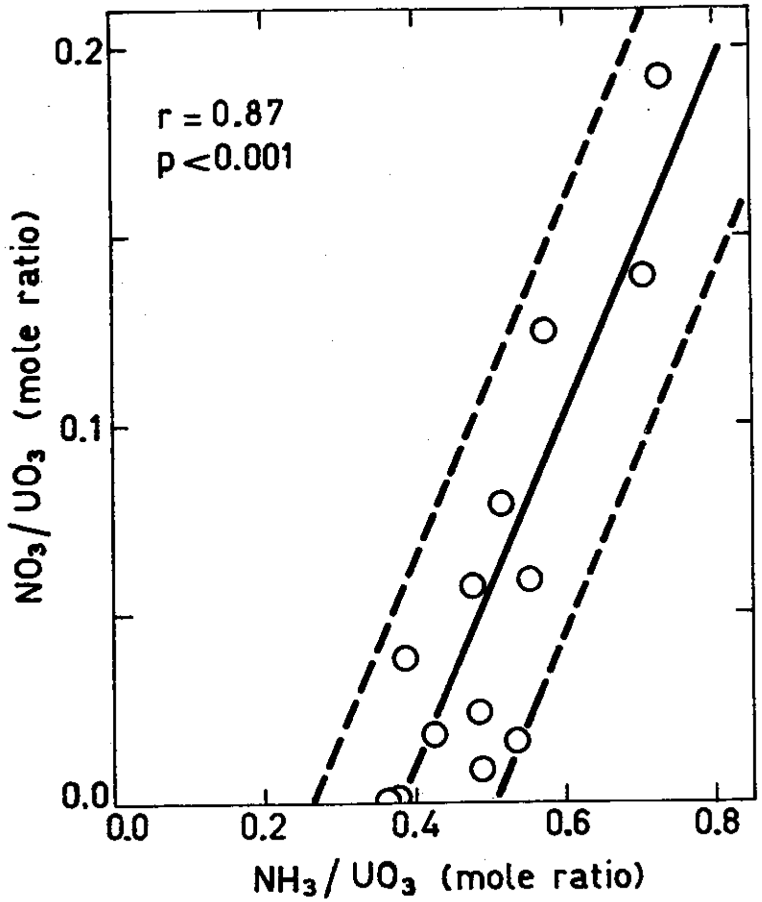


FIGURE 3. CORRELATION BETWEEN THE TOTAL AMMONIA AND NITRATE CONTENT OF THE AU POWDERS

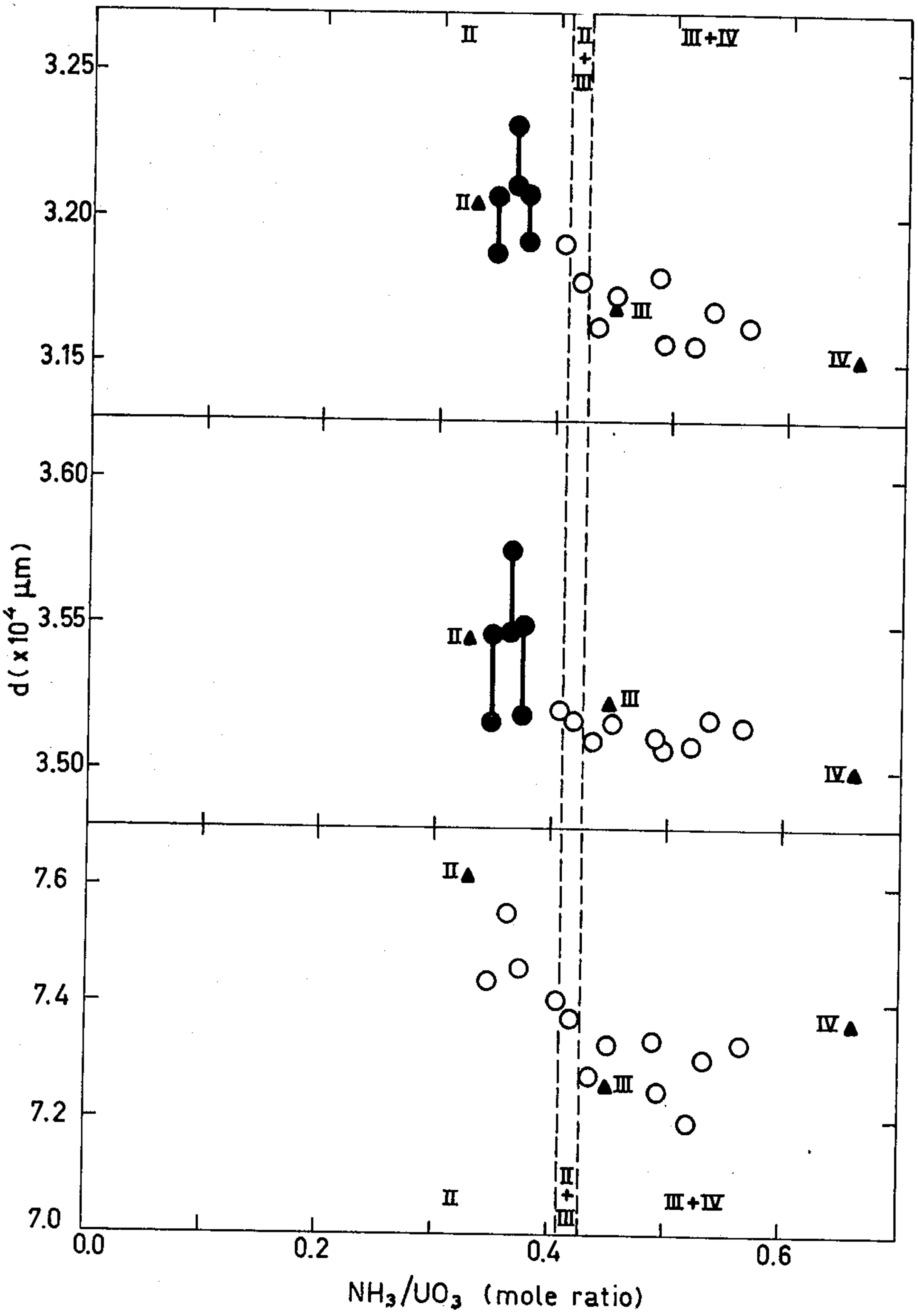
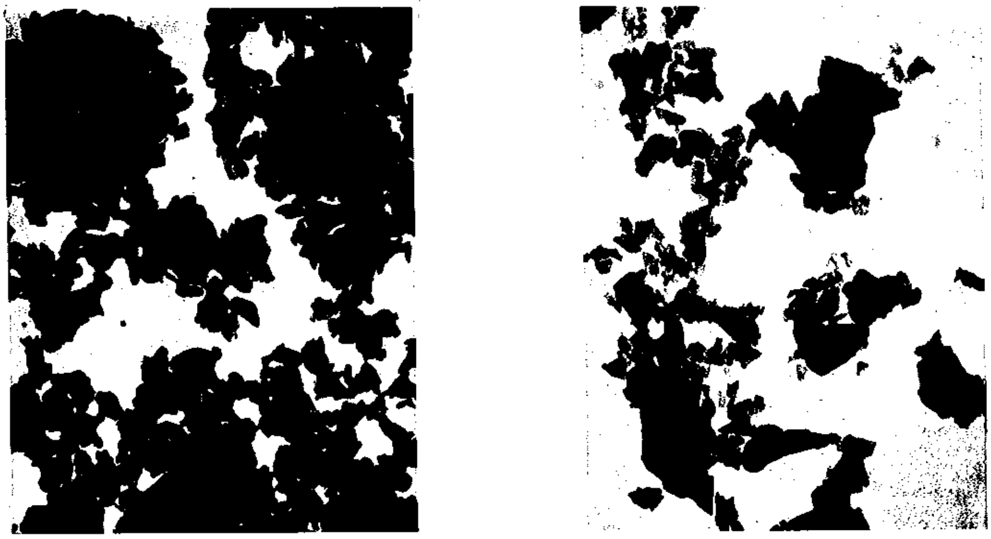
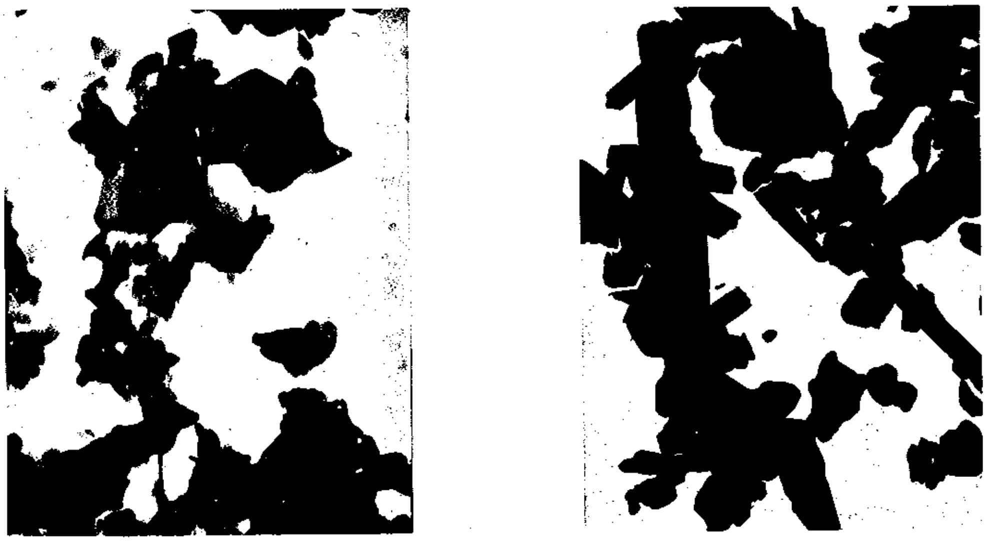


FIGURE 4. VARIATION IN THE d-SPACING OF THE THREE MOST INTENSIVE X-RAY DIFFRACTION PEAKS IN AU WITH AMMONIA CONTENT. SOLID POINTS REPRESENT ALPHA-DOUBLET SEPARATION



pH 10 (x 40 000) pH 8.6 (x 40 000)



pH 7.1 (x 40 000) pH 4.2 (x 10 000)

FIGURE 5. ELECTRON MICROGRAPHS OF AU POWDERS PRECIPITATED AT pH 4.2, 7.1, 8.6 AND 10.

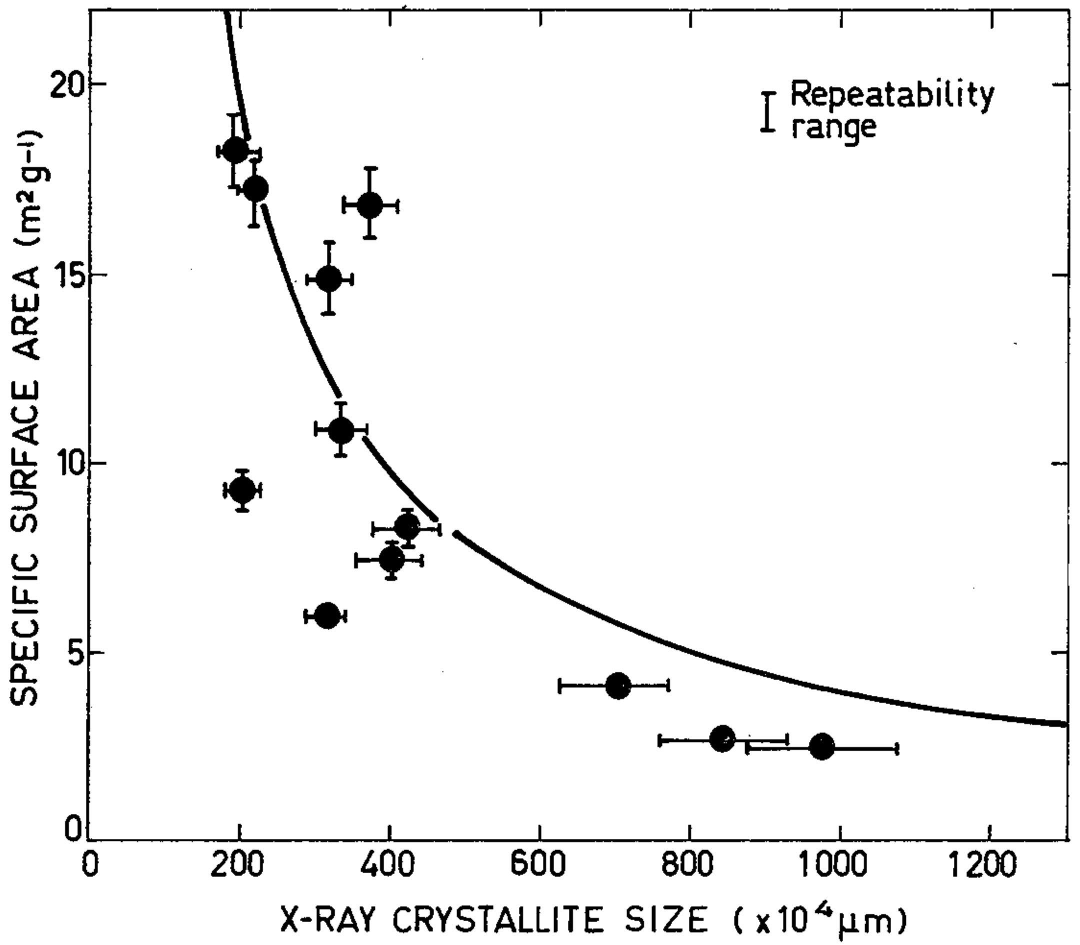


FIGURE 6. RELATIONSHIP BETWEEN THE X-RAY CRYSTALLITE SIZE AND SPECIFIC SURFACE AREA FOR THE AU POWDERS

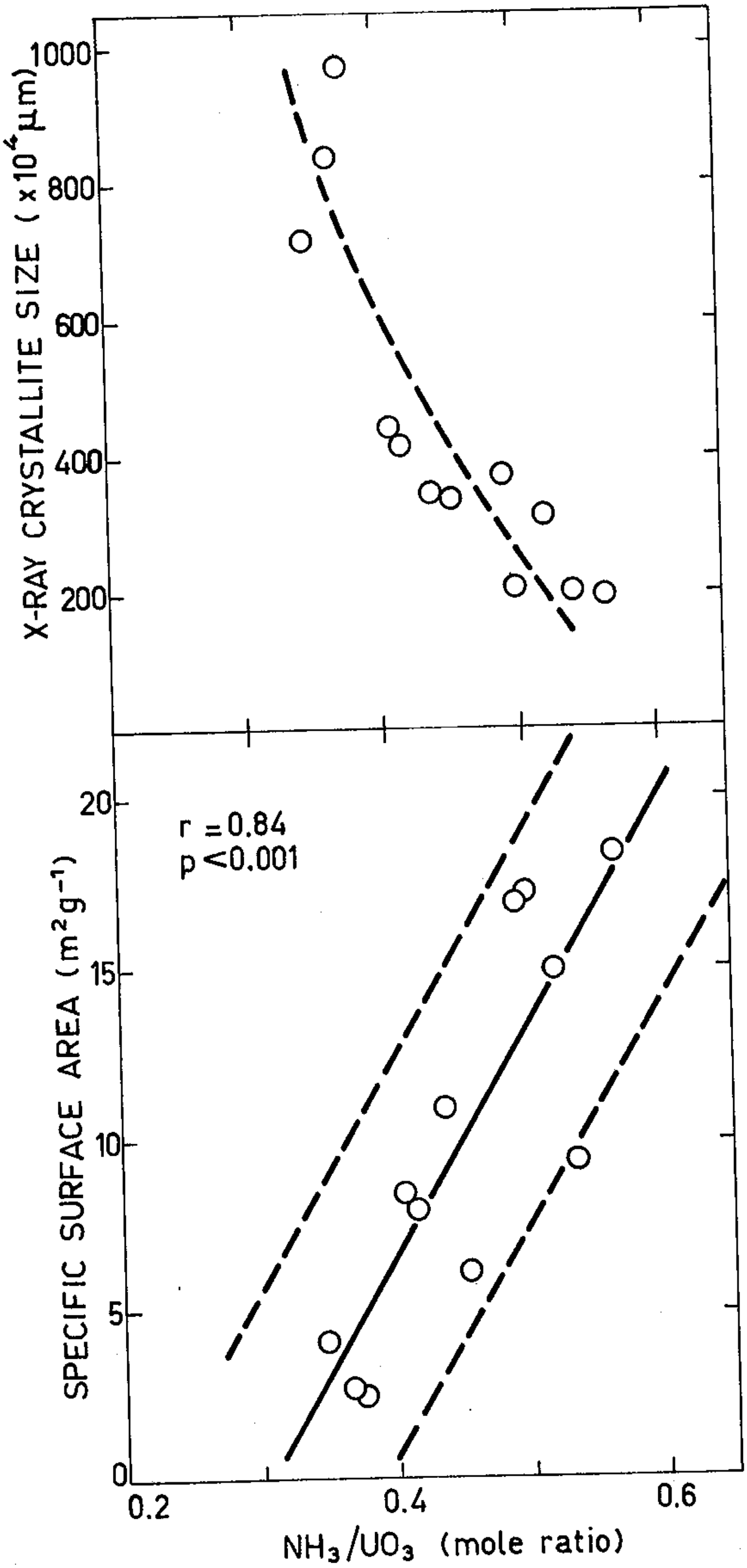


FIGURE 7. CORRELATION BETWEEN THE COMBINED AMMONIA CONTENT AND THE SPECIFIC SURFACE AREA AND X-RAY CRYSTALLITE SIZE OF THE AU POWDERS