

**COMPARATIVE STUDY OF THE ALKALINITY OF SOME ASHED PLANT RESIDUE AND THEIR POTENTIAL TO LIBERATE AMMONIA FROM POULTRY MANURE.**

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**Abstract**

*The alkaline strengths of ash samples of eight plant residues obtained as waste from refuse dump sites and farms within Minna metropolis and environs were determined by pH titrimetric method. The relative strength of each ash sample was compared with a standardised sodium hydroxide solution by calculating the amount of ammonia liberated from the same mass of a sample of poultry manure. The titration curves produced two equivalence points that were similar to that obtained with a solution containing a mixture of carbonate and hydrogen carbonate ions. An initial reaction between the acid and the alkaline metal oxides followed by that involving the other constituent sparingly soluble oxides is proposed. Relative strengths of the ash samples ranged from 1.4 percent (rice husks) to 15.4 percent (plantain husks). The results justified the various uses of plant residue ash in Nigeria and elsewhere.*

**Introduction**

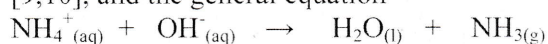
In crop production, wastes are generated from the stage of harvesting, when plant parts are often left on farmlands, to that when the farm products are processed and the un-edible parts discarded. However, not all wastes remain so, unless no use is found for them. The most common usage of plant residue had been as animal feedstuff, bedding material in livestock pens, mulching material and compost manure. In some localities in Nigeria, and perhaps elsewhere, the plant residue is burnt and the ash provides a raw material for the production of black soap. Plant residue ash has also been sprinkled on young growing crops to prevent attack by pests or fungi, and applied to soils high in acidity to ameliorate the adverse reactions [1]. Clearly, a large proportion of plant residues from agricultural activities find usage in many sectors of the economy, including agriculture itself.

Similarly, in the poultry industry, large amounts of wastes are produced, most of which are channeled into crop production as manure to improve soil fertility. Recycling of poultry waste as feedstuff for other animals has also been reported in the literature [2]. Animal waste is a source of ammonia; the decay of the organic matter in the litter generates ammonia

[3,4], the rate of which is influenced by the room temperature and the litter's moisture content. The presence of bedding material such as saw dust also contributes significantly to the mineralization process [5,6]. It is therefore common to smell the gas in poultry houses, especially when the pens are left uncleaned for long periods of time. Thus, useful as the litter may be, it could constitute an environmental nuisance and a health hazard if not properly disposed of.

The art of soap making is an age-long practice in traditional African communities. Before the industrial revolution that saw the emergence of modern technologies and techniques of soap making, the African harnessed local raw materials, which otherwise were waste products of agricultural activities, to produce soap. Vegetable oil and plant residue ash constituted the major ingredients for the necessary saponification reaction [7,8]. Among the plant residues were plantain or banana peels and palm fruit bunch, which are still in use today in many parts of Nigeria. In the presence of water, the ash which contains the oxides of alkali and other metals, is hydrolysed, producing the alkali hydroxides needed for the reaction. It follows, therefore,

that the hydroxyl ion required to react with an ammonium ion in the conventional laboratory preparation of ammonia could readily be supplied when water is added to a mixture of plant tissue ash and a substance that can provide an ammonium ion in aqueous solution. Poultry manure is a readily available and cheap natural source of this ion [3,4] from which some substantial amounts of ammonia may be obtained. Therefore, it is predictable that on boiling this mixture, ammonia should constitute one of the products. The ammonium ion provides the Bronsted acid that reacts with the hydroxyl ion generated from the hydrolysis [9,10], and the general equation



applies to this aqueous system due mainly to the well known high solubility of all ammonium salts.

The objective of this paper is to determine the alkalinity of some plant residue ash and their relative potential to release ammonia from poultry manure.

### Materials and Methods

The plant residues, including plantain husks, groundnut shells, used broom sticks, saw dust, palm fruit bunch, rice husks, maize cobs and rice straws, were collected during the crop harvesting season (October to November, 2004). Palm fruit bunches and plantain husks were obtained from foodstuff traders in Minna Central market and premises of local restaurants, respectively. The premises of peasant farmers and rice mills were the sources of groundnut shells, maize cobs, and rice husks. Old broomsticks and sawdust were sourced from homes and the Bosso Village Saw Mill, respectively. The rice straws, on the other hand, were collected from farms where they had been left after harvesting. In all cases, samples were taken from three locations and only the most recently discarded "clean" residues were chosen for sampling to avoid the need for washing as a pre-treatment step. The poultry manure was obtained from three dumpsites of the Niger State Livestock Company, Minna.

Following sample collection, the plant residues were sun-dried (fresh samples only) for several days. They were then chopped (palm fruit

bunch was first split into shreds), mixed to give a bulked sample of each location, and then air-dried in the laboratory. A portion of each plant tissue was placed in a crucible and burnt using a bunsen flame. Complete ashing was finally carried out in a Gallenkamp Tactical 308 muffle furnace at about 570°C. The three samples of poultry manure were also bulked and thoroughly mixed after stones and other foreign matter had been removed.

### Alkalinity of the ashed plant residue

About 1g of the ash sample was weighed and placed in a 100cm<sup>3</sup> beaker. 20cm<sup>3</sup> of de-ionised distilled water was added, swirled to ensure dispersal and then titrated with a 0.05M HCl solution using Kent EIL 7045/46 pH meter. The suspension was stirred by means of a magnetic stirrer as the titrant was added.

### Basic strengths of ash samples

In order to determine the relative basic strengths of the ash samples, the amount of ammonia each of these liberated from a given mass of poultry manure was compared with that liberated from the same mass of the poultry manure by a measured amount of a standardised sodium hydroxide solution. About 1g of poultry manure was placed in a 250cm<sup>3</sup> beaker and 50cm<sup>3</sup> of 0.182M NaOH solution was added and swirled. The suspension was then boiled until evolution of ammonia ceased (i.e. when the characteristic brown precipitate was no longer produced on a filter paper moistened with Nessler's reagent). The mixture was allowed to cool, filtered and a measured portion of the filtrate was titrated with the standardised acid as before. The procedure was repeated using about 2g of the ash sample and 50cm<sup>3</sup> water in place of the standard sodium hydroxide solution. The difference between the titre values, with and without the poultry manure gave the volume of acid that was equivalent to the amount of alkali required to liberate the available ammonia from the manure.

### Calculation of relative strength of ash

The ionic equation above was used to obtain expressions that provided the data in Table 1. The moles of alkali  $m_A$  (equal to moles of

reacted acid) that liberated the quantity of ammonia was calculated from the expression,

$$m_A = m_S - m_R$$

where  $m_S$  is the moles of alkali ( equal to moles of reacted acid) initially present, and  $m_R$  is the moles of residual alkali (equal to moles of reacted acid) in the mixture of standard sodium hydroxide solution (or ash) and manure suspension.

Relative strengths of the ash samples were calculated by relating the moles of ammonia liberated by each ash sample to that liberated by the mole equivalent of 1g standard sodium hydroxide solution as follows:

$$\text{Relative strength (\%)} = 100m_A/m_H$$

where  $m_H$  is the moles of ammonia liberated by the standard alkali solution.

### Results and Discussion

The pH values of the aqueous suspensions of the ash samples ranged from 8.06 in rice husks to 12.50 in palm fruit bunch, from which it is clear that the samples were reasonably alkaline in their reactions. The curves of pH against volume of 0.05M HCl solution obtained in

respect of the different samples of ash are shown in Figure 1. The corresponding first derivative of the curves in respect of palm fruit bunch and maize cob are presented in Figure 2. They produced two peaks that were similar to those of curves of the titration involving an acid and an aqueous solution of carbonate and hydrogen carbonate [11]. To explain the occurrence of two equivalence points, recourse may be made to the suggestion that the ash contained all the oxides of the metal ions present in the plant residue, including the alkali and alkaline earth metal oxides. In the presence of water, hydrolysis occurs, producing the hydroxyl ions which are neutralized by the acid. However, it is obvious that the alkali metal oxides are more susceptible to hydrolysis than the alkaline earth metal oxides. As a consequence of the slow hydrolysis, due certainly to the sparingly soluble nature of the alkaline earth and other oxides, complete neutralization of the mixture was delayed, probably until complete dissociation of these less soluble oxides was achieved.

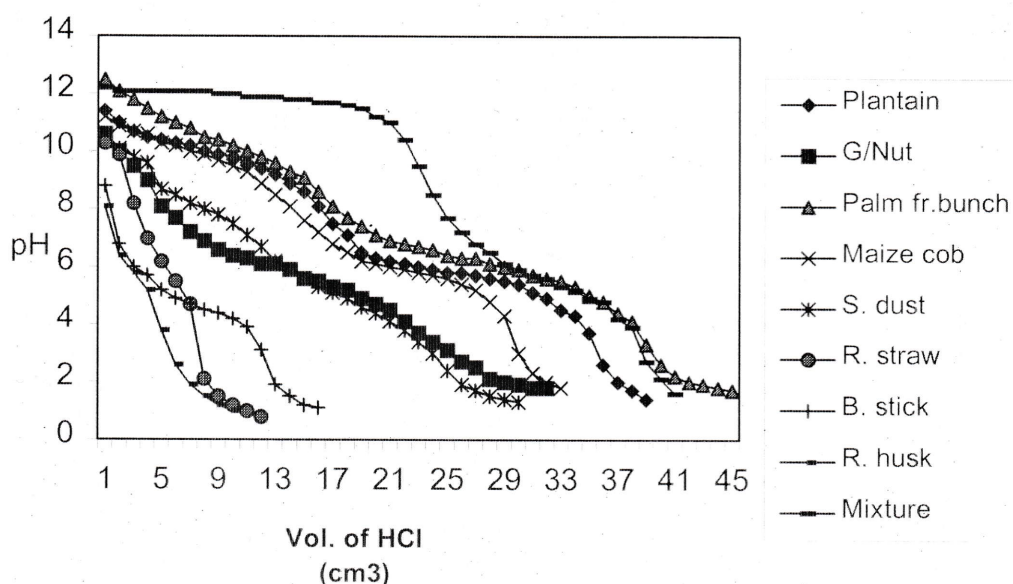


Fig. 1 Curve of 5% ash suspension against 0.05mol/dm<sup>3</sup> HCl

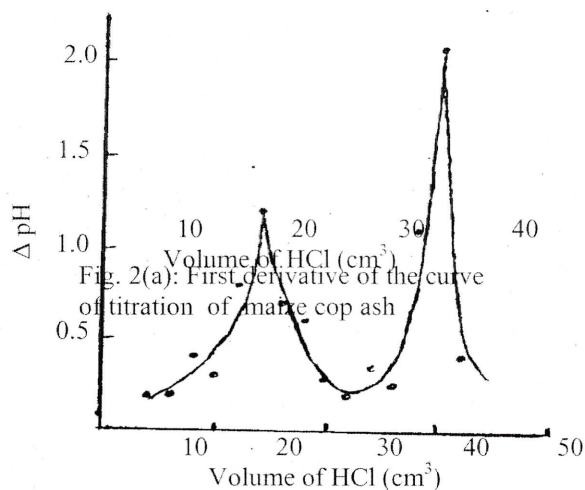


Fig. 2(a): First derivative of the curve of titration of maize ash

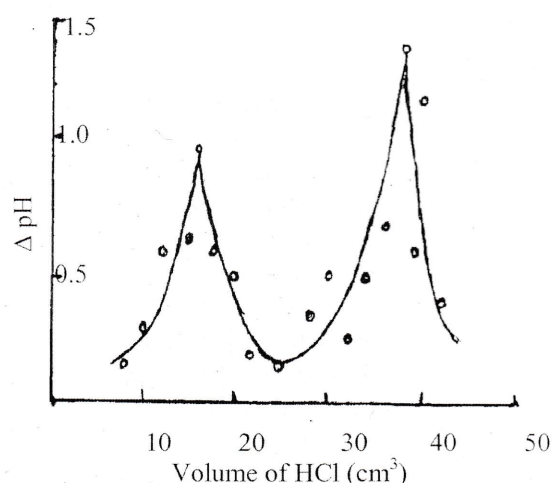


Fig. 2(b): First derivative of the curve of titration of palm bunch ash suspension

Furthermore, it may be reasonable to infer that the first equivalence point corresponds to that of the neutralization of the alkaline hydroxides, and in addition, part of the hydroxyl ions resulting from the initial dissociation of the alkaline earth hydroxides. Later dissociation process, which is believed to be aided by the removal of the OH<sup>-</sup> ions initially present by the titrant, produced the final hydroxyl ions that gave rise to the second equivalence point, thereby signaling the complete neutralization of the suspension. In order to ascertain that, in fact, this was the case in support of the occurrence of two equivalence points, a standard mixture of sodium hydroxide and calcium oxide suspension was subjected to the same determination, resulting in the curve identified as "mixture" in the legend of Figure 1. The first equivalence point of this curve corresponded to about  $1.19 \times 10^{-3}$  moles of OH<sup>-</sup> ions in the suspension; a value which was about 2.6 times of that expected. The additional quantity amounting to about  $7.24 \times 10^{-4}$  moles of alkalinity at this point is accounted for by the contribution from the initial dissociation of the calcium oxide. Thus,

the presence of sparingly soluble metal oxides in plant ash probably shifts the equivalence point of the titration of its aqueous suspension to higher values, thereby producing a second equivalence point. Therefore, these oxides (the sparingly soluble) do contribute significantly to the total basic reaction of the ash of plant tissues, making them more valuable ingredients in the production of black soap and in other uses where alkalinity is an important property.

The relative strengths of ash samples, calculated as percent of moles of standard acid which reacted with a given mass of ash, as against that needed to react with the same mass of sodium hydroxide, are presented in Table 1. Clearly, plantain peels ash takes the lead. This probably explains the preference for this plant tissue ash in the local soap industry. For the same reason of its relatively high alkalinity, palm fruit bunch ash enjoys equal popularity for the same application. The availability and abundance of the plant sources (plantain and palm tree) in some parts of Nigeria is an added advantage in their usage.

**Table 1: Relative Strengths ( $\text{g}^{-1}$  NaOH) of plant residue ash**

Plant ash	PH of suspension	Moles of $\text{NH}_3$ liberated	Relative Strength (%)
Plantain husks	11.39	$5.84 \times 10^{-3}$	15.4
Palm fruit bunch	12.50	$3.46 \times 10^{-3}$	13.4
Maize cobs	11.16	$2.73 \times 10^{-3}$	10.9
Broom sticks	8.80	$1.18 \times 10^{-3}$	4.7
Grandaunt shells	10.58	$1.06 \times 10^{-3}$	4.2
Saw dust	10.88	$1.09 \times 10^{-3}$	4.4
Rice stalks	10.45	$7.3 \times 10^{-4}$	2.9
Rice husks	8.06	$3.6 \times 10^{-4}$	1.4

Some comment on the amounts of ammonia liberated by the different ash samples seems imperative. The values obtained in this determination may have been influenced by a number of factors. Core among them was the degree of decay of the manure. This was tested and confirmed by using two samples of poultry waste that had been dumped two weeks and five weeks, respectively, prior to collection.  $1.76 \times 10^{-2}$  and  $2.08 \times 10^{-2}$  mol.  $\text{dm}^{-3}$   $\text{NH}_3$ , respectively were liberated on boiling with the standardised NaOH solution. A second major factor has to do with the alkalinity of the ash. This value depends to a large extent on the mineralogy of the soil on which the source plant grew and the capacity of the plant concerned to accumulate sodium and potassium ions in its tissues [12,13]. Kubmarawa and Atiko [7] reported a value of 18.9 percent as the alkalinity of maize cob ash. Of no less importance too is the degree of completeness of combustion of the plant residue.

Perhaps the discussion will be incomplete without a comment on the pH values of the aqueous suspensions and their relevance to the reactions of ash. In this respect attention is drawn to the plots of Figure 1 which enabled a visual comparison of the relative alkaline strengths of the ash samples to be made more readily than with those of their first derivatives. It is evident from Table 1 and Fig. 1 that the total basic strength of the ash may not necessarily depend on the pH of its aqueous suspension. Although the sparingly soluble constituent oxides could make important contribution to the total basic reaction of the ash concerned, the situation may be different with respect to the pH values.

A careful examination of the first equivalence points of the curves in particular, indicates that those samples of ash with higher pH values probably contain higher amounts of the alkaline oxides. These oxides provided the hydroxyl ions that reacted to liberate ammonia. Expectedly, the order of magnitude of the amount of ammonia liberated and, therefore, the relative strengths of the samples of ash should correspond to that of the volume of standard acid required to reach the first equivalence point. This was found to be true, but only in respect of four samples (plantain peels, palm fruit bunch, maize cobs and rice husks). The reason for the disruption of this order may be explained by the differences in the amount of the little contribution of  $\text{OH}^-$  ions to the pool by the sparingly soluble oxides. These oxides, in spite of their not being crucial to the pH values of the aqueous suspensions of the plant tissue ash, may actually have produced enough hydroxyl ions in the samples concerned to overturn the expected order. The final pertinent point that needs to be made is related to the observed low ease of neutralization of the sparingly soluble oxides compared to their alkaline metal counterparts. Agronomically speaking, this is an important property. It means that the elevation of pH of acidic soils to which plant ash is applied can be sustained for relatively longer periods of time.

### Conclusion

The ash of the plant residues employed in this determination were sufficiently basic and had the capacity to liberate ammonia from poultry manure. The results justify the use of plant ash in the local soap industry and in agriculture for

the amelioration of acidic soils. The pH of the aqueous suspensions of the ash probably only indicated the relative amounts of alkaline metal oxides in the samples rather than the total basic strength. This view was supported by the absence of a corresponding order of magnitude between pH and total basic strength of the samples of ash. Differential release of OH<sup>-</sup> ions by the sparingly soluble oxides may be responsible for this behaviour. Therefore, pH may not be an ultimate parameter in the choice of plant ash to employ for a particular purpose where alkalinity is the relevant ingredient.

Finally, the results provide an insight into the need to explore the possibility of small scale production of ammonia from these local raw materials.

#### References

1. B.T. Kang and A. Sajjanpense (1990), Effect of heating on properties of some soils from Southern Nigeria and growth of rice. *Plant and Soil Analysis*, **55**, 85-95.
2. P. Hobson and A.G. Hashimoto (1990), Digestibility of untreated and chemical treated animal excreta for ruminants: A review. *J. Biological Wastes*, **31**, 17 – 36.
3. J.H. Seinfeld (1986). *Atmospheric Chemistry and Physics of Pollution*. John Wiley and Sons. New York. pp. 12 – 16.
4. P. Matthews (1992), *Advanced Chemistry*. Cambridge University Press. pp. 607 – 609.
5. P.A.E. Ako, A.S. Adebajo and A.L. Fadipe (2001), Effect of pH, concentration, and time on the extractability of manure phosphorus in aqueous medium. *Nig. J. Appl. Sci.*, **19**, 69-75.
6. P.A.E. Ako, A.S. Adebajo, A.L. Fadipe and M.M. Ndamitso (2003), Extractability of potassium from some organic manures in aqueous medium and the effect of pH, time and concentration. *J. Appl. Sci. Environ. Mgt.*, **7**, 51 - 162.
7. D. Kubmarawa and R. Atiko (2000), Production of soap from locally sourced caustic alkali and oils. *J. Chem. Soc Nig.*, **25**, 76-78.
8. A.O. Kuye and C. Okorie (1990), Factors affecting the lixiviation of palm bunch ash as a source of alkali for soap production. *Ifè Jour. Tech.*, **2**, 33-37.
9. P.W. Atkins (1989), *General Chemistry*. Scientific American Books. New York. pp. 518 – 519.
10. R.I. Caret, K.J. Denniston and J.J. Topping (1997), *Principles and Applications of Inorganic, Organic and Biological Chemistry*. 2<sup>nd</sup> Edition. McGraw-Hill. New York. pp 200 – 201.
11. C.T. Kenner (1971), *Analytical Determinations and Separations: A Textbook in Quantitative Analysis*. The Macmillan Company. New York. pp. 159 – 162.
12. Z Liu; Q.Q. Zhu and L.H. Tang (1983), Micronutrients in the main soils of China. *Soil Sci.*, **135**, 40-46.
13. V.V. Rendig and H.M. Taylor (1989), *Principles of Soil-Plant Interrelationships*. McGraw-Hill Publishing Company. New York. pp.141-165.