Method of Washing Filter Papers to Remove Nitrogen Contamination

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Summary: Whatman filter papers contain inorganic nitrogen impurities (NH_4, NO_3 and NO_2-N) which could introduce an error into the analysis of coal mine soils. The levels of inorganic nitrogen in the filter paper were found to be 3.1 to 5.3 mg of NH_4-N and 12.1 mg of NO_3-N/kg of filter paper. In order to minimise the effects of inorganic nitrogen contained in the filter papers, it is necessary to wash them with 0.5 M H_2SO_4, rinse them with deionised water and dry them prior to use for filtration.

Introduction

Many procedures for the measurement of ammonium and nitrate nitrogen in soils and other materials call for extracting these ions with a salt solution and then filtering the extract through filter paper (Keeney and Nelson) [1]. Seldom, however, do these procedures caution about the possibility of the filter paper contributing to significant analytical errors.

In the past several research workers have reported that filter paper can cause errors in the measurements of ammonium or nitrate-N in filtered extracts. Leitch and Wells [2] obtained erratic results in total and non-protein nitrogen determinations due to filtration through standard filter papers and have recommended the use of small sintered glass filters. O'Halmhain and O'Danachair [3] reported variable amounts of ammonia content in analytical filter papers, and re-emphasized the necessity of carrying out blank determinations with all reagents, including filter papers, and of taking the blank determination through all the stages of the analysis. Muneta [4] tested different grades of filter papers for nitrate-N. He found that some qualitative papers contained enough nitrate-N to cause significant errors in the analysis of cured meats, whereas quantitative (low-ash or ashless) grade contained very little or no nitrate-N. Hattori et al [5] tested different grades and batches of filter papers for ammonium-N content by eluting them with 1.3 M (10%) potassium chloride solution and analysing the leachate. They found a significant variation among grades, batches within grade, packages within batches, and papers within package and recommended the use of filter papers with low ammonium-N content. Sparrow and Masiak [6] tested filter papers for ammonium and nitrate-N and reported a significant amount of ammonium or nitrate-N in many filter papers. They have recommended the pre-washing of cellulose filter papers with water or 2 M potassium chloride solution. Khan [7] has also found variable amounts of ammonium in various batches of filter papers and recommended the prewashing of Whatman No. 40 filter papers with 50 cm^3 of 0.5 M potassium sulphate solution in two equal successive portions, and then rinsing twice with deionized water and drying for 4 hours at 70°C.

Since coal mine soils contain very low levels of inorganic nitrogen compared to normal soils, therefore a very small amount of impurity in the filter paper can cause a considerable analytical error. So it was considered essential to wash the filter paper prior to filtration.

Washing of filter papers with 0.5 M potassium sulphate solution prior to use for removing sources of nitrogen contamination was one acceptable procedure in our laboratory as recommended by Khan [7], but such a procedure was rather tedious and time-consuming due to preparation of ammonia-free potassium sulphate solution. Moreover, the method seemed to be expensive as Whatman No. 40 filter papers are more costly compared with Whatman filter paper No. 2.

The objectives of this study were (i) to measure ammonium, nitrate and nitrite-N eluted from Whatman filter paper No. 2 (ii) To compare

M hydrochloric acid, 0.5 M sulphuric acid and 0.5 M potassium sulphate as washing solutions for filter papers prior to use for filtration.

Materials and Methods

Two boxes of Whatman filter paper No. 2 (W. & R. Balston Ltd) having the same control No. (5141/131) and size (12.5 cm) were used during this study.

Reagents

Analar grade reagents and nitrogen-free deionized water were used throughout.

1/ Sulphuric acid (0.5 M) 2/ Hydrochloric acid (1 M) 3/ Potassium sulphate solution (0.5 M)

0.5 M sulphuric acid and M hydrochloric acid were made from the bottles of the corresponding concentrated acid. Ammonium-free potassium sulphate solution was prepared according to the method proposed by Khan [7].

Procedure

In order to compare acid washing of filter paper with that of potassium sulphate, 20 filter papers were selected at random from a box and each one folded separately into a clean and dry plastic funnel. Ten filter papers were leached with 0.5 M sulphuric acid and another set of ten with 0.5 M potassium sulphate. 50 cm^3 of washing solution was filtered through each filter paper in two equal successive portions of 25 cm^3 each. The filtrate of each portion of washing solution was collected separately into clean dry plastic bottles and kept for ammonium, nitrite and nitrate-N determinations. Nitrate-N was determined only in potassium sulphate filtrate, because it was impossible to determine nitrate-N in the acid filtrates. The filter papers were rinsed with deionized water to remove any residue of washing solution. In the case of potassium sulphate washing, two rinsings with deionized water were given, but for acid washed filters 3-4 rinsings with deionized water were required until the filter papers were acid free. Litmus test paper was used for this purpose. Then the washed filter papers, along with funnels, were dried in a 70°C oven for 4 hours. After drying each of the 10 filters were again leached with 50 cm^3 0.5 M potassium sulphate solution and the leachate was analysed for ammonium, nitrite and nitrate-N by a Technicon Auto Analyser for any N contamination left after washing.

For comparing sulphuric acid washing of filter papers with that of hydrochloric acid, 20 filter papers were selected at random from the 2nd box. A set of 10 filters was used for each acid wash, 50 cm^{-3} of acid in two equal portions of 25 cm^3 were used for washing each filter paper by following the above procedure.

In this case the acid filtrates were not collected. After rinsing with deionized water and drying in the oven, each of 10 filters were leached with 50 cm^3 of 0.5 M potassium sulphate solution and the leachate was analysed for ammonium, nitrite and nitrate nitrogen.

Results and Discussion

The amount of nitrite nitrogen extracted from each filter paper was very small. The ammonium and nitrate nitrogen eluted from filter papers by the washing solution was calculated and divided by the average weight of a filter paper to obtain the amounts of ammonium or nitrate nitrogen per unit weight of filter paper. Each value in the tables represents the mean of 10 replicate analyses. The data were analysed on a micro computer using a statistical program. A 'T test' was applied to determine the significance of differences between means with probability of 0.05, 0.01 and 0.001.

A summary of ammonium and nitrate nitrogen extracted by 0.5 M sulphuric acid or 0.5 M potassium sulphate solution from unwashed filter papers, and the nitrogen extracted from washed filters by 0.5 M potassium sulphate solution is given in Table-1. Whatman filter paper No. 2 used in this experiment contained a range of 3.1 to 5.3 mg of ammonium-N and 12.1 mg of nitrate-N/kg of filter paper. This is large enough to cause significant errors in the analysis of coal mine soils which are already very low in such forms of nitrogen. As far as the efficiency of 0.5 M sulphuric acid or 0.5 M potassium sulphate as washing solutions was concerned, the former also seemed to be a good washing solution. There was no significant difference in the amounts of ammonium nitrogen extracted from

filters washed by either of the above two washing solutions. The amount of NO_3-N left after washing in the filters paper was significantly more in potassium sulphate washed filters than sulphuric acid washed filter papers.

Table-1: The NH_4 and NO_3-N contents of washed and unwashed filter papers.

Washing Solution	NH_4-N (mg N/kg paper)		NO_3-N (mg N/kg paper)	
	unwashed	washed	unwashed	washed
0.5M H_2SO_4	5.3	0.9	-	0.0
0.5 M K_2SO_4	3.1	0.7	12.1	0.2
		NS		***

T Test on N content of washed filters
NS Not significant
*** $P < 0.001$

The results presented in Table-2 indicate the ammonium and nitrate nitrogen extracted by 0.5 M potassium sulphate solution from filter papers after washing with 0.5 M sulphuric acid or M hydrochloric acid from a 2nd box of Whatman filter paper No. 2. There was no significant difference in ammonium nitrogen content extracted from the washed filters with either of the two different acids, but in this case 0.5 M sulphuric acid proved to be a comparatively better washing solution than hydrochloric acid, due to the significant amount of nitrate nitrogen left in the filters washed with M hydrochloric acid. The higher content of nitrate nitrogen in the hydrochloric acid washed filter papers was probably due to chloride ion interference in the nitrate-N determination, because of some of the washing solution remaining in the filter papers and then being extracted with 0.5 M potassium sulphate solution.

Table-2: Ammonium and nitrate nitrogen extracted by 0.5 M potassium sulphate solution from filter papers washed with 0.5 M sulphuric acid or M hydrochloric acid.

Washing Solution	NH_4-N (mg N/kg paper)		NO_3-N (mgN/kg paper)	
	unwashed	washed	unwashed	washed
0.5 M H_2SO_4	-	1.2	-	0.7
M HCl	-	1.4	-	0.8
		NS		**

T Test on N contetn of washed filters
NS Not significant
** $P < 0.01$

The difference between 0 and 0.2 mg of nitrate-N/kg filter paper (Table-1) and between 0.7 and 0.8 mg/kg filter paper (Table-2) though statistically significant, seemed to be not more than the estimated random error of the method. The estimated random error of the method for nitrate-N determination on the Technicon Auto Analyzer was from $\pm$ 0.1 to $\pm$ 0.2 ppm, therefore, the difference was not big enough to matter.

The selection of 70°C drying for 4 hours was based on the findings of Khan [7], who reported that drying at this temperature for 4 hours will not affect the ammonium levels in the filter papers.

It is concluded that washing of the Whatman filter paper No. 2 with 0.5 M sulphuric acid prior to use could be an acceptable procedure for eliminating this source of error, but care must be taken that acid washed filter paper must be rinsed at least 3 times with deionized water, in order to make it acid-free, otherwise this may result in acid leachates that could not be analysed accurately.

Method of filter Paper Washing

0.5 M sulphuric acid was prepared from Analar grade concentrated acid using nitrogen-free deionized water.

Each filter paper was folded separately into a clean and dry plastic funnel. 50 cm^3 0.5 M sulphuric acid was filtered through each filter paper in two equal successive portions of 25 cm^3 each. Then the acid washed filter papers werer insed 3 times with deionized water to wash away any acid left in the filter paper. Care was taken to make sure that the filter papers were made acid-free. Litmus test paper was used for this purpose. Then the washed filter papers alongwith funnels were dried for 4 hours in a 70°C oven before using for filtration.

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