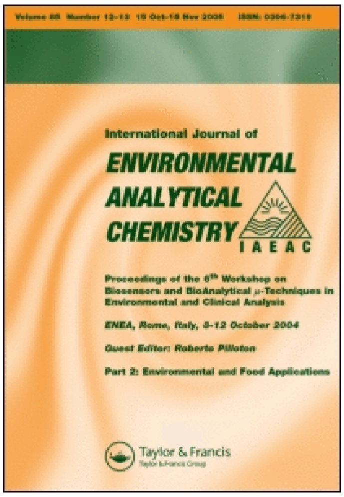

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# A Comparison of Two Methods for the Determination of Total Acidity of Humic Substances

A. Piccolo[a]; L. Camici[a]
[a] Istituto Sperimentale per lo Studio e la Difesa del Suolo, Firenze, Italy

**To cite this Article** Piccolo, A. and Camici, L.(1990) 'A Comparison of Two Methods for the Determination of Total Acidity of Humic Substances', International Journal of Environmental Analytical Chemistry, 41: 1, 65 — 69

**To link to this Article: DOI:** 10.1080/03067319008030530

**URL:** http://dx.doi.org/10.1080/03067319008030530

*Int. J. Environ. Anal. Chem.*, Vol. 41, pp. 65–69
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# A COMPARISON OF TWO METHODS FOR THE DETERMINATION OF TOTAL ACIDITY OF HUMIC SUBSTANCES

A. PICCOLO and L. CAMICI

*Istituto Sperimentale per lo Studio e la Difesa del Suolo,*
*Piazza M. D'Azeglio 30, Firenze, Italy*

(*Received 28 February 1989; in final form 6 March 1990*)

Two methods of total acidity determination for humic substances are compared: (1) the traditional barium hydroxide method, and (2) a direct potentiometric titration after elution of humic substances through a cation exchange resin. The first method always gave higher results than the second method. A poor analytical precision observed for the former method was attributed to carbonation. Low-molecular-weight phenolic acids of known total acidity were also analyzed by the two methods. The first method most likely underestimates results when weakly acidic compounds do not precipitate as barium salts. The low values shown by the second method are partially due to adsorption of humic material on the resin and, possibly, to insufficient protonation of acidic groups during resin elution.

KEY WORDS: Humic substances, total acidity, barium hydroxide, potentiometric titration, exchange resin.

## INTRODUCTION

Humic substances are naturally occurring macromolecular compounds which are present in terrestrial and aquatic environments. Their environmental importance lies in the capacity of interacting with metals and organic chemicals, thereby influencing the mobility of pollutants. Since the reactivity of humic substances mainly depends on the content of acidic functional groups, it is essential to determine their acidity in order to predict their environmental behaviour.

A number of analytical methods have been proposed[1,2] for the determination of total acidity of humic substances. The most widely used indirect barium hydroxide method was originally designed for use with coal and later adapted to humic substances.[1] A known amount of barium hydroxide solution at pH 13 is equilibrated with a sample of humic substances, so that even compounds with the weakest acidic group will be dissociated and precipitated as barium salts. The unreacted $OH^-$ are filtered off and then titrated at $pH = 8.4$. The difference in sample and blank titrations is used to calculate total acidity. An underestimation of total acidity may occur if any compounds with weakly acidic groups in the reaction mixture remain in solution rather than precipitate as barium salts; these solutes will be re-protonated during titration to $pH = 8.4$.[3,4]

Another method is the discontinuous direct potentiometric titration.[5,6] This is performed by firstly acidifying humic substances to $pH = 4$ and, then, titrating to the equivalence point.[7] An overestimation of total acidity has been reported for

**Table 1** Elemental composition and ash content of humic extracts

| *Sample* | % *C* | % *H* | % *N* | % *Ash* |
|---|---|---|---|---|
| $HA_1A_1$ | 34.1 | 3.9 | 3.7 | 30.1 |
| $HA_1A_2$ | 52.1 | 5.3 | 7.7 | 31.3 |
| $HA_1A_3$ | 30.9 | 3.9 | 4.9 | 20.5 |
| $HA_2A_{11}$ | 56.8 | 4.5 | 5.2 | 9.0 |
| $HA_2A_{12}$ | 48.5 | 3.3 | 4.6 | 7.5 |
| $HA_2A_{13}$ | 55.8 | 3.9 | 4.2 | 8.5 |
| $HA_3A_1$ | 53.4 | 4.4 | 5.1 | 1.1 |
| $HA_3A_2$ | 55.4 | 3.2 | 4.8 | 1.0 |
| $HA_3A_3$ | 56.6 | 3.9 | 5.3 | 1.9 |
| $HE_1L$ | 50.3 | 4.3 | 0.0 | 8.3 |
| $HE_1Lh$ | 57.6 | 3.3 | 0.0 | 1.0 |
| $HE_2L$ | 47.8 | 3.2 | 1.1 | 3.0 |
| $HE_2Lh$ | 60.1 | 4.0 | 0.0 | 2.2 |

this method due to the possibly occurring hydrolysis[8,9] and oxidation[10] reactions and electrode interferences[4] in strongly alkaline solution. These inconveniences may also play a role in the barium hydroxide method.

Some authors have used strong ion exchange resins to obtain metal-humic complexes[11] and fully protonated purified humic substances.[12,13] A humic substance solution eluted through such an ion exchange resin may have a pH as low as 3. When this solution is titrated potentiometrically with alkali, a value for total acidity is obtained.[13] This method has the advantage, over discontinuous titration, that it eliminates the initial electrolyte addition and better controls ionic strength.[6] It also minimizes the occurrence of hydrolysis reactions which may take place with the barium hydroxide method.

The aim of the present study was to compare the barium hydroxide method with the direct potentiometric titration after cation exchange resin elution in order to evaluate the reliability of the latter method for total acidity determination of humic substances.

## MATERIALS AND METHODS

Humic acids were extracted as outlined by Stevenson[2] from the horizons of three volcanic soil profiles of the caldera of Vico near Rome. The soils were classified as Typic Xeroumbert ($HA_1$), and Typic Dystrandepts ($HA_2$ and $HA_3$). Additional humic extracts were obtained by extracting a commercial North Dakota leonardite (Mammoth Co.), with DMSO ($HE_1$) and acetone ($HE_2$) as outlined by Piccolo.[14] All humic samples were purified by a HCl–HF treatment, dialyzed (3.5 K cut-off membrane) against water, and freeze-dried.[14] The humic extracts obtained with dipolar aprotic solvents were further hydrolyzed by refluxing for 24 h in 6 M HCl ($HE_1h$ and $HE_2h$). The elemental composition and ash content of the humic extracts are reported in Table 1.

**Table 2** Total acidities and relative standard deviations (in parentheses) of humic samples as determined by the barium hydroxide method (A) and by potentiometric titration (B)[a]

| *Sample* | *A* | *B* | $B_{corr}$[b] | *A/B* | $A/B_{corr}$ |
|---|---|---|---|---|---|
| $HA_1A_1$ | 6.57 (0.04) | 1.77 (0.03) | 3.68 | 3.71 | 1.78 |
| $HA_1A_2$ | 7.52 (0.16) | 2.47 (0.08) | 3.36 | 3.04 | 2.24 |
| $HA_1Bw$ | 2.94 (0.14) | 1.45 (0.01) | 2.87 | 2.03 | 1.02 |
| $HA_2A_{11}$ | 7.64 (0.28) | 3.76 (0.07) | 4.03 | 2.03 | 1.90 |
| $HA_2A_{12}$ | 9.44 (1.28) | 4.62 (0.08) | 5.05 | 2.03 | 1.87 |
| $HA_2A_{13}$ | 8.31 (0.01) | 5.33 (0.08) | 5.99 | 1.56 | 1.39 |
| $HA_3A_1$ | 8.46 (0.21) | 4.00 (0.06) | 4.99 | 2.12 | 1.70 |
| $HA_3A_2$ | 8.68 (0.43) | 4.15 (0.04) | 4.41 | 2.09 | 1.97 |
| $HA_3A_3$ | 8.32 (0.66) | 4.13 (0.03) | 4.59 | 2.01 | 1.81 |
| $HE_1L$ | 7.02 (0.04) | 2.96 (0.06) | 4.92 | 2.37 | 1.43 |
| $HE_1Lh$ | 8.23 (0.08) | 4.07 (0.12) | 4.07 | 2.02 | 2.02 |
| $HE_2L$ | 7.75 (0.05) | 3.27 (0.03) | 6.54 | 1.53 | 1.19 |
| $HE_2Lh$ | 7.12 (0.16) | 3.10 (0.02) | 4.78 | 1.73 | 1.49 |

[a] Values for total acidities are in mol/kg.

[b] Values of B corrected for the amount adsorbed on the resin.

The barium hydroxide method as reported by Schnitzer and Khan[1] was adopted in this study. Samples used for direct potentiometric titration were first dissolved by adding 0.5 M KOH until a pH of 7 was reached and then eluted through a column containing a fully-protonated Dowex 50X4-400 cation exchange resin. The eluted solution was adjusted to a final volume of 2000 ml containing 1 mg/ml of humic material. To 50 ml of this solution, 2.5 M KCl was added to maintain an ionic strength of 0.1. An Orion Research 960 automatic titration apparatus was used to titrate the humic solution up to pH = 9 with 0.1 M NaOH (reference 7). Three replicate measurements of each sample were made for both methods.

## RESULTS AND DISCUSSION

The values found for total acidity by both methods, and their standard deviations, are reported in Table 2. All samples showed higher (1.5–2.7-fold) total acidities by the barium hydroxide method than by potentiometric titration after cation-exchange resin elution. This result may be attributed to the formation of insoluble barium carbonate during filtration of the unreacted strongly alkaline barium hydroxide solution. The dissolved atmospheric $CO_2$ consumes titratable $OH^-$, thereby causing an overestimation of the total acidity determination. This evident phenomenon (increased turbidity of filtrates) was probably the reason for the high standard deviation and, hence, for the poor precision of this method compared to the second method (Table 2). However, since total acidity is obtained by calculating differences with the titration of blank samples, carbonation should not affect the accuracy of the method.

An explanation for the low values found by the second method is the possible

**Table 3** Total acidities and relative standard deviations (in parentheses) of some low-molecular-weight phenolic acids as determined by the barium hydroxide method (A) and by potentiometric titration (B)[a]

| *Sample* | *A* | *B* | $B_{corr}$[b] | *Calculated value* |
|---|---|---|---|---|
| Gallic acid | 21.0 (1.6) | 9.7 (0.2) | 9.9 | 23.5 |
| Protocatechuic acid | 8.6 (0.5) | 9.8 (0.2) | 10.4 | 19.5 |
| 2,4-Dihydroxybenzoic acid | 14.7 (1.4) | 10.5 (0.1) | 10.9 | 19.5 |
| Phloroglucinol | 1.6 (0.5) | 12.6 (0.3) | 15.6 | 23.8 |

[a] Values for total acidities are in mol/kg.

[b] Values of B corrected for the amount adsorbed on the resin.

adsorption of humic material on the ion exchange resin with the consequent reduction of titratable humic substances. This was verified by freeze-drying an aliquot of the eluate and weighing the freeze-dried material. The difference between the amount of humic substances initially added to the column and that eluted per ml from the resin represented the adsorbed material. Total acidities by direct titration were recalculated on the basis of the adsorbed material; the corrected values are reported in Table 2. Adsorption on the resin was found to have occurred for all humic samples, although not to the same extent. $HA_1Bw$ and $HE_2L$ showed values comparable to those of the barium hydroxide method, whereas the rest of the corrected figures remained up to 2.2 times lower than those of the first method. That is, adsorption of humic materials on the resin cannot, entirely account for the differences in total acidity. Low values found with this method may also be explained by an insufficient protonation of humic substances during elution from the resin. This would mean a reduced number of titratable protons on the humic substances and a consequent underestimation of total acidity. Such behaviour would be independent of primary structure and configuration of humic material since it was shown by all humic samples in this study.

To evaluate the accuracy of each method, low-molecular-weight phenols and phenolic acids of known total acidity were also analyzed (Table 3). Both methods gave total acidities lower than those calculated from the structure of the analyzed compounds. This indicates that, for the barium hydroxide method, the carbonation effect did not overestimate total acidities, whereas a large underestimation occurred when some of the low-molecular-weight compounds (protocatechuic acid and phloroglucinol) failed to form insoluble barium salts, thereby confirming a source of error in the method.[3,4] The low values obtained by direct potentiometric titration and even those corrected for resin adsorption show that this method significantly underestimates total acidities.

## CONCLUSIONS

Our results show that the barium hydroxide method is a more accurate procedure, although less precise, than the direct potentiometric titration for total acidity determination of humic substances. The poor precision can be attributed to the variable carbonation of strongly alkaline barium hydroxide solution, while the formation of soluble barium salts of low-molecular-weight weakly acidic compounds may be a source of negative errors. The direct potentiometric titration after protonation of humic substances by ion-exchange resin elution, underestimates total acidities and is not suitable for analysis despite a good precision and a reduced risk of interferences.[4,10] The low values should not wholly be attributed to adsorption on the resin but, rather, to a limited protonation of humic substances during elution through the resin.

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