

STATISTICAL ANALYSIS AND CHEMOMETRIC METHODS

Gravimetric Quantification of Hydrophobic Fulvic Acids in Lignite Material Using Acetone

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This study evaluated the gravimetric quantification of fulvic components in lignite material. The current standard method considered only components soluble in both alkali and acid solutions and adsorbed to a hydrophobic resin (DAX-8) at pH 1, identified as hydrophobic fulvic acids (HFA). HFA were desorbed using 0.1 M sodium hydroxide (NaOH) and run through a cation exchange resin (IR-120) to remove Na ions. HFA were quantified gravimetrically, including ash corrections. Steps involving IR-120, however, resulted in a large volume of analytical solution and a significant time of analysis, which became a disadvantage of this method. A modification to this method was proposed by replacing NaOH with acetone to desorb HFA from DAX-8. IR-120 was not required, and a smaller volume of analytical solution was produced. Gravimetric, Fourier transform infrared (FTIR), and ionic analyses were completed in this study. Both standard and modified methods resulted in the presence of hydrophobic neutrals within the quantification of HFA. Acetone at 50% strength produced HFA results corresponding to those of NaOH. An adequate regeneration of DAX-8 was achieved using the modified method but not with the standard method. The modified method produced higher ash contents, but they did not affect its accuracy. This method significantly reduced the overall analytical time. This study showed the potential of acetone as a desorbing agent in the gravimetric quantification of HFA in lignite material.

In this method, HS were defined as major organic constituent of natural organic matter consisting of complex heterogeneous mixtures of carbon-based substances formed by biochemical reactions during the decay and transformation of plant and microbial remains. Fulvic components were identified as the ones soluble in both alkali and acid solutions and adsorbed to a hydrophobic resin (DAX-8) at pH 1. They were defined as hydrophobic fulvic acids (HFA). The principles of this method can be summarized as follows (2). (1) Alkali extraction was completed under anoxic conditions to reduce oxidation of the analytical sample during extraction. (2) Alkali extracted portions of HS insoluble in strongly acidic solutions and precipitated from alkali extract in acid solutions of pH 1 were defined as humic acids (HA). (3) Alkali extracted portions of HS soluble in both alkali and acid aqueous solutions were defined as fulvic fraction (FF). (4) Materials composed of <0.75% elemental sulfur (S) soluble in aqueous alkaline and acid solutions and adsorbed at pH 1 onto a polymeric adsorbent resin of moderate polarity designed for adsorption of amphiphilic compounds having molecular weights typical of FF were defined as HFA. The resin of interest would be DAX-8 of methacrylic ester material. (5) Ash-free gravimetric analyses were completed for both HA and HFA. Because this study only discusses HFA, analytical steps related to HA were all skipped.

In this method, HFA were adsorbed by DAX-8, desorbed using sodium hydroxide (NaOH), cleaned from Na ions using a cation exchange resin of hydrogen form (IR-120), and then quantified gravimetrically including ash corrections (1, 2). However, steps involving IR-120 produced a significant volume of analytical solution (to be partially reduced using a Rotovap prior to the gravimetric analysis) and required significant time for the analysis (including its regeneration). This could become a disadvantage of this method with respect to its acceptance within the commercial community.

An effort was made, therefore, to modify this standard method so that the total analytical time could be significantly reduced. In this modified method, acetone replaced NaOH to desorb HFA from DAX-8. Acetone was selected because it is one of the most common and effective organic solvents available in the market with the following advantages: It is miscible in water, able to bind both polar and nonpolar materials, and has a lower boiling point than that of water, as presented in Table 1 (5, 6). *Note:* Acetone was previously found producing a low desorption rate of HS material in DAX-2 resin of styrene divinylbenzene material (7). This could be caused by (1) the fact that this resin was less effective than that of DAX-8 with respect to FF-related applications (8), (2) a higher pumping rate during resin adsorption (9), (3) that HS material was not first dissolved in water at high pH, (4) that HA was not separated from HFA, and (5) slightly higher pH of the analytical solution (approximately 2 compared to 1; 2).

Gravimetric analysis is one of the most accurate and practical methods to quantify fulvic components in materials containing humic substances (HS). Among several methods available in the industry, the Humic Products Trade Association (HPTA) method (1) and ISO 19822 (2) were the best to date, as they included improvements over the previous methods (3, 4). ISO 19822 was developed from the HPTA method with several changes in its analytical steps. In terms of principles, both were identical. Throughout this study, these methods are identified as the “standard method.”

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Table 1. Acetone properties

Parameter	Value
Molecular weight	58.08 g/mol
Empirical formula	C ₃ H ₆ O
Boiling point	56°C
Freezing point	-95°C
Specific gravity	0.79
Water solubility	Total (miscible)
Solubility parameter	10.0
Polarity (water = 100)	35.5
pH	7.0
Acetone	99.8%
Water	0.2%
Methanol	<0.02%
Alcohol	<0.005%
Aldehyde	<0.002%

In this modified method, NaOH would not be added during DAX-8 desorption, and therefore, IR-120 would not be required. Steps involving IR-120, including its regeneration, would all be skipped. A smaller volume of analytical solution with a lower boiling point would be produced, such that a Rotovap would not be necessary. The solution could directly be quantified for HFA.

The substitution of NaOH with acetone might, however, have effects on the principles. The following items needed to be addressed and carefully evaluated in this study. (1) NaOH would exchange (i.e., desorb) all organic acid anions, whereas acetone would dissolve (i.e., desorb) all organic components, resulting in the possible presence of hydrophobic neutrals (HN) within the quantification of HFA (7, 10, 11). (2) During DAX-8 regeneration, steps using deionized (DI) water and hydrochloric acid (HCl) might not be sufficient because of the possible presence of HN within the analytical solution. (3) Because IR-120 would not be required, Na cations added during alkali extraction would still be in the analytical solution, which might affect the accuracy of gravimetric analysis.

A laboratory study was completed with the main objective of evaluating the use of acetone as the desorbing agent and whether this modified method could speed up the total analytical time while still maintaining its principles and accuracy.

Experimental

A lignite sample from North Dakota was used in this study. Its chemical compositions were analyzed by a third-party laboratory and presented in Table 2 (12). Thirty-four runs were completed

in this study, including 28 runs using the lignite sample and 6 blank runs using DI water. The standard method was used in 11 runs, and the modified method was used in 23 runs. Four runs were analyzed by a third-party laboratory for Fourier transform infrared (FTIR) spectra, 28 runs were quantified gravimetrically in-house for HFA by Canadian Humalite International Inc., and 2 runs were analyzed using inductively coupled plasma (ICP) by a third-party laboratory for Na and chloride (Cl) ions (see Table 3 for the Experimental Protocol). Run 1 (Lignite-Standard-1) represented the first run completed in this study, i.e., the first replication of the lignite sample using the standard method; Run 16 (Lignite-Modified75%-4) represented the 16th run completed in this study, i.e., the fourth replication of the lignite sample using the modified method at 75% acetone strength; Run 32 (Blank-Modified50%-5) represented the 32nd run completed in this study, i.e., the fifth replication of DI water using the modified method at 50% acetone strength; and so on.

Differences in analytical steps between the two methods were as follows. The standard method used NaOH at 0.1 M strength as a desorbing agent, IR-120 to remove Na ions from the analytical solution, and a Rotovap to partially evaporate the solution prior to its gravimetric analysis. For the regeneration of DAX-8, two columns of DI water, one column of 0.1 M HCl, and one column of DI water were used in each of 11 runs. The modified method used acetone at 25, 50, and 75% strengths as the desorbing agent. IR-120 was not required, and no partial evaporation using a Rotovap was needed. For the regeneration of DAX-8, two columns of DI water, one column of 0.1 M HCl, and one column of DI water were used in each of 12 runs (Runs 2–4, 7–12, and 14–16), and two columns of DI water, one column of 0.1 M HCl, one column of 50% acetone, and one column of DI water were used in each of 11 runs (Runs 20–24, 26, and 28–32).

Principles of this modified method would be evaluated using FTIR and gravimetric analyses. These would determine the nature of organic components being analyzed (i.e., HFA and/or HN). Many articles have been published differentiating FTIR spectra of hydrophobic acids and HN generated from different water and soil samples (10, 13). A more straightforward approach was taken in this study by considering only absorbance readings at 2922 and 1701 cm⁻¹, representing C-H and C=O groups, respectively. The C-H group was assumed to be responsible for the negative charge behavior at pH of <7, as in the case of HFA. The C=O group was assumed to be responsible for the neutral charge behavior, as in the case of HN (14, 15). Both analyses would also determine the performance of DAX-8 regeneration steps.

The accuracy of this modified method would be evaluated using gravimetric and ionic analyses. The gravimetric analysis would determine the right strength of acetone as the desorbing agent, corresponding to HFA results produced by the standard method using 0.1 M NaOH. It would also show the amount of

Table 2. Lignite sample chemical compositions^a

Element	C	H	O	N	S	Ash									
Ultimate analysis – dry matter, %	56.52	4.63	22.41	1.34	1.15	13.95									
Element	Al	Ca	Fe	K	Mg	Na	P	Si	Ti						
ICP analysis – dry matter, %	5.72	10.52	3.17	0.29	2.46	1.41	<0.01	0.70	0.35						
Element	As	Ba	Cd	Cl	Cu	Cr	Hg	Mn	Mo	Ni	Pb	Sr	Th	Zn	Zr
ICP analysis – dry matter, ppm	11	403	1	3	75	10	0.09	445	9	14	28	1157	165	50	178

^a Moisture content = 12.13%.

Table 3. Experimental protocol

Run	Identification	Sample	DAX-8 desorption	Analysis
1	Lignite-Standard-1	Lignite	0.1 M NaOH	HFA
2	Lignite-Modified25%-1	Lignite	25% acetone	HFA
3	Lignite-Modified50%-1	Lignite	50% acetone	HFA
4	Lignite-Modified75%-1	Lignite	75% acetone	HFA
5	Lignite-Standard-2	Lignite	0.1 M NaOH	HFA
6	Lignite-Standard-3	Lignite	0.1 M NaOH	HFA
7	Lignite-Modified25%-2	Lignite	25% acetone	HFA
8	Lignite-Modified50%-2	Lignite	50% acetone	HFA
9	Lignite-Modified50%-3	Lignite	50% acetone	HFA
10	Lignite-modified75%-2	Lignite	75% acetone	HFA
11	Lignite-Modified25%-3	Lignite	25% acetone	HFA
12	Lignite-Modified75%-3	Lignite	75% acetone	HFA
13	Lignite-Standard-4	Lignite	0.1 M NaOH	HFA
14	Lignite-Modified25%-4	Lignite	25% acetone	HFA
15	Lignite-Modified50%-4	Lignite	50% acetone	HFA
16	Lignite-Modified75%-4	Lignite	75% acetone	HFA
17	Lignite-Standard-5	Lignite	0.1 M NaOH	FTIR
18	Lignite-Standard-6	Lignite	0.1 M NaOH	HFA
19	Lignite-Standard-7	Lignite	0.1 M NaOH	HFA
20	Blank-Modified50%-1	DI water	50% acetone	HFA
21	Blank-Modified50%-2	DI water	50% acetone	FTIR
22	Lignite-Modified50%-5	Lignite	50% acetone	FTIR
23	Lignite-Modified50%-6	Lignite	50% acetone	HFA
24	Lignite-Modified50%-7	Lignite	50% acetone	HFA
25	Lignite-Standard-8	Lignite	0.1 M NaOH	HFA
26	Blank-Modified50%-3	DI water	50% acetone	FTIR
27	Lignite-Standard-9	Lignite	0.1 M NaOH	HFA
28	Blank-Modified50%-4	DI water	50% acetone	HFA
29	Lignite-Modified50%-8	Lignite	50% acetone	HFA
30	Lignite-Modified50%-9	Lignite	50% acetone	HFA
31	Lignite-Modified50%-10	Lignite	50% acetone	Na + Cl
32	Blank-Modified50%-5	DI water	50% acetone	HFA
33	Lignite-Standard-10	Lignite	0.1 M NaOH	Na + Cl
34	Blank-Standard-1	DI water	0.1 M NaOH	HFA

ash within the analytical solution, which was later confirmed using the ICP analysis on Na and Cl ions. The effect of ash on the HFA gravimetric analysis could therefore be evaluated.

The practicality of this modified method would be evaluated based on time consumed for each analytical step to be completed. Changes made to DAX-8 regeneration steps might result in a slightly longer analytical time, whereas skipping analytical steps on IR-120 and a Rotovap would result in a significant time reduction.

Chemical Requirements

(a) *NaOH*.—Laboratory grade, 95% minimum purity (16), made into 0.1 M solution.

(b) *HCl*.—Laboratory grade, 31% strength (17), made into 0.1, 1.0, and 6.0 M solutions.

(c) *Silver nitrate (AgNO₃)*.—Laboratory grade, 0.1 M strength (18).

(d) *Nitrogen gas*.—Laboratory grade, 99.9% purity (19).

(e) *Acetone*.—Laboratory grade, 99.8% purity (5, 6), made into 25, 50, and 75% strengths.

(f) *Supelco Supelite DAX-8 resin 21567-U*.—The hydrophobic resin stored in methanol (20).

(g) *Amberlite IR120 resin hydrogen form 10322*.—The cation exchange resin (21).

(h) *DI water*.

Equipment Requirements

(a) *Mortar, pestle, and combustion crucible (100 mL) of ceramic material*.

(b) *Analytical balance*.—220 g capacity, ± 0.1 mg precision.

(c) *Sieve analyzer*.—With No. 200 mesh screen.

(d) *Erlenmeyer flasks (1000 mL), centrifuge tubes (50 mL), chromatography column of 4 × 25 cm (for DAX-8 resin), chromatography column of 5 × 60 cm (for IR-120), and beaker (50 mL) of glass material*.

(e) *Spectrophotometer cuvettes (5 mL) of plastic material*.

(f) *Magnetic stir plate and magnetic bar*.

(g) *Plastic paraffin films*.

(h) *Centrifuge*.—Relative centrifugal force ≥ 1500 .

(i) *pH Meter*.—Unit accuracy ± 0.01 .

(j) *Peristaltic pump and tubing*.—5 L/min pumping rate.

(k) *Spectrophotometer*.—350 nm wavelength, ± 0.005 unit accuracy.

(l) *Rotovap*.—400 mL capacity.

(m) *Drying oven*.—120°C capacity, ± 0.1 °C accuracy.

(n) *Combustion oven*.—1000°C capacity, ± 1 °C accuracy.

(o) *Desiccator*.—4 L capacity.

(p) *Plastic beaker (4 L)*.

(q) *Manual stirrer*.

(r) *Timer*.

Procedures

(a) *Alkali extraction*.—Approximately 5 g lignite sample was pulverized to pass through mesh No. 200 of U.S. standard sieve size and placed in a crucible and then in a drying oven to a constant weight at 62 ± 3 °C. Approximately 2.5 g dry sample was weighed and put it in a 1000 mL Erlenmeyer flask, followed by 0.1 M NaOH and DI water to make 1000 mL final solution. *Note:* For each blank run, DI water of the same weight replaced the lignite sample. The flask was placed on a magnetic plate with a magnetic bar inside. Air was replaced with nitrogen gas, the flask was covered with a plastic paraffin film, and the solution was mixed for 16 h. The content was transferred to centrifuge tubes and centrifuged for 30 min. Precipitates were discarded, and supernatant (containing HA and FF) was collected in a 1000 mL Erlenmeyer flask. A pH probe was inserted into the solution, and 6.0 M HCl was added until pH = 1.0 ± 0.1 . The flask was covered with a plastic paraffin film and mixed for 1 h. pH Was occasionally checked until it was stable for 5 min and was readjusted when necessary. The solution was left unstirred for 4 h. The content was transferred to centrifuge tubes and centrifuged for 30 min. Precipitates (containing HA, not needed in this study) were discarded. The analytical solution (containing FF)

was transferred to a 1000 mL Erlenmeyer flask and analyzed for HFA.

(b) *HFA analysis*.—(1) Fifty mL DAX-8 was packed in a 4×25 cm column. It was firstly rinsed with DI water, then with 0.1 M NaOH and 0.1 M HCl three times alternatingly, then soaked with DI water. HFA was adsorbed by pumping FF solution from top of the column. Effluent was discarded from the bottom. The resin was washed using DI water after two column volumes. HFA was then desorbed back to the analytical solution using the following steps.

(2) *Standard method*.—NaOH of 0.1 M strength was pumped from the top until three column volumes. Effluent was collected from the bottom and poured from the top into a 5×60 cm column filled with 500 mL IR-120 to flow by gravity until two column volumes. The column was washed with 500 mL DI water and added to the solution. The analytical solution was concentrated using a Rotovap to approximately 50 mL at $62 \pm 3^\circ\text{C}$. The solution was transferred to a ceramic crucible, placed inside a drying oven for to a constant weight at $62 \pm 3^\circ\text{C}$, and then placed in a desiccator to cool to room temperature and recorded for its weight. The crucible was later put in a combustion oven for 4 h at 500°C and then placed in a desiccator to cool to room temperature and recorded for its weight. Calculations were as follows: Percent ash = (weight of material after combustion \div weight of dry material) \times 100, and Percent HFA = [(weight of material after drying – ash) \div weight of dry material] \times 100.

(3) *Modified method*.—Acetone of the desired strength (25, 50, or 75%) was pumped from the top until three column volumes. Effluent was collected from the bottom in a 1000 mL Erlenmeyer flask, placed inside a drying oven to approximately 100 mL at $62 \pm 3^\circ\text{C}$, transferred to a ceramic crucible, then placed inside the oven to a constant weight at the same temperature. It was then placed in a desiccator to cool to room temperature and recorded for its weight. The crucible was later put in a combustion oven for 4 h at 500°C and then placed in a desiccator to cool to room temperature and was recorded for its weight. Calculations were the same as in (2) above.

(4) *DAX-8 regeneration for the standard method*.—Two columns of DI water, one column of 0.1 M HCl, and one column of DI water were pumped from the top. For the modified method of 12 runs (Runs 2–4, 7–12, and 14–16), two columns of DI water, one column of 0.1 M HCl, and one column of DI water were pumped from top. For the modified method of 11 runs (Runs 20–24, 26, and 28–32), two columns of DI water, one column of 0.1 M HCl, one column of 50% acetone, and one column of DI water were pumped from the top.

(5) *IR-120 regeneration for the standard method*.—The resin was poured into a 4 L beaker, covered with 1.0 M HCl, and left for 30 min with occasional stirring once every 5 min. It was rinsed with DI water, stirred for 15 s, and left for 5 min. These steps were repeated until the rinse water was free from Cl ions, as per the following steps. Ten milliliters of rinse water was put in a 50 mL beaker, and then two drops of 0.1 M AgNO_3 were added until no precipitates or changes in color were observed. For the modified method, this resin would not be required, and the whole series of steps could be skipped.

During the quantification of HFA, the analytical time to complete each step was recorded. Changes in the modified method compared with the standard method included the use of acetone as an additional step during DAX-8 regeneration and the omission of IR-120 and a Rotovap.

Table 4. FTIR results

Run	Identification	pH	Group		Ratio
			C-H	C=O	
17 ^a	Lignite-Standard-5	2.6	0.193	0.131	1.47
21 ^b	DI water-Modified50%-2		Blank		
22 ^c	Lignite-Modified50%-5	2.8	0.194	0.176	1.10
26 ^d	DI water-modified50%-3	2.4	0.100	0.070	1.43

^a Completed after one run of Lignite-Modified75%.

^b Completed after one run of DI water-Modified50%.

^c Completed after one run DI water-Modified50%.

^d Completed after one run of Lignite-Standard.

Results

Using the FTIR analysis, spectra for Runs 17, 21, 22, and 26 were generated within absorbance ranges of 600–4000 cm^{-1} . Run 21 had no identifiable (blank) spectra. Others showed the presence of polysaccharides, C=C, COO^- stretch, C=O of COOH, aliphatic C-H stretch, C-H stretch, and O-H stretch, typically observed for samples containing fulvic components. pH values of these three runs were 2.6, 2.8, and 2.4, respectively (14, 15). For the identification of HFA and HN, only readings at 2922 and 1701 cm^{-1} were discussed. Run 17 showed 0.193 and 0.131 readings (ratio = 1.47), Run 22 showed 0.194 and 0.176 readings (ratio = 1.10), and Run 26 showed 0.100 and 0.070 readings (ratio = 1.43), respectively (see Table 4). For pH values of <7 , higher ratio values indicated that the organic components were more to the negative charge behavior, whereas lower values were more to the neutral side (14, 15).

Using the gravimetric analysis for the lignite sample, acetone at 50% strength (Runs 3, 8, 9, 15, 23, 24, 29, and 30) produced HFA results [mean = 2.31%, SD = 0.227%, and coefficient of variation (CV) = 9.8%] corresponding to those of the standard method of Runs 1, 5, 6, 13, 18, 19, 25, and 27 (mean = 2.38%, SD = 0.203%, and CV = 8.5%). Acetone at 25% strength (Runs 2, 7, 11, and 14) produced lower results (mean = 1.88%, SD = 0.144%, and CV = 7.7%). Acetone at 75% strength (Runs 4, 10, 12, and 16) produced higher results (mean = 2.47%, SD = 0.343%, and CV = 13.9%). Run 20 produced 0.35% HFA. Run 28 produced 0.16% HFA. Run 32 produced 0.03% HFA. Run 34 produced 0.31% HFA (see Table 5).

For the gravimetric analysis of the lignite sample, acetone at 50% strength of Runs 3, 8, 9, 15, 23, 24, 29, and 30 produced higher ash contents (mean = 34.81%, SD = 9.058%, and CV = 26.0%) than those of the standard method of Runs 1, 5, 6, 13, 18, 19, 25, and 27 (mean = 16.03%, SD = 5.286%, and CV = 32.9%). Run 32 (Blank-Modified50%-5) and Run 34 (Blank-Standard-1) produced 92.34 and 64.68% ash, respectively (see Table 6). The ionic analysis using ICP found 11.2 mg/L Na and 43.7 mg/L Cl for Run 31 (Lignite-Modified50%-10), whereas Run 33 (Lignite-Standard-10) contained 1.9 and 14.6 mg/L, respectively, as presented in Table 7 (22).

From 28 runs of gravimetric analysis on HFA, the average total analytical time to complete one analysis using the standard method was 57 h. The addition of acetone during DAX-8 desorption in the modified method increased its analytical time by 0.25 h. The omission of IR-120 and a Rotovap in the

Table 5. HFA results

Run	Identification	Mean, %	SD, %	CV, %
1, 5, 6, 13, 18, 19, 25, 27	Lignite-Standard-1, 2, 3, 4, 6, 7, 8, 9	2.38	0.203	8.5
2, 7, 11, 14	Lignite-Modified25%-1, 2, 3, 4	1.88	0.144	7.7
3, 8, 9, 15, 23, 24, 29, 30	Lignite-Modified50%-1, 2, 3, 4, 6, 7, 8, 9	2.31	0.227	9.8
4, 10, 12, 16	Lignite-Modified75%-1, 2, 3, 4	2.47	0.343	13.9
20 ^a	DI water-Modified50%-1	0.35	NA ^b	NA
28 ^c	DI water-Modified50%-4	0.16	NA	NA
32 ^d	DI water-Modified50%-5	0.03	NA	NA
34 ^e	DI water-Standard-1	0.31	NA	NA

^a Completed after three consecutive runs of Lignite-Standard.

^b NA = Not available.

^c Completed after one run of Lignite-Standard.

^d Completed after three consecutive runs of Lignite-Modified50%.

^e Completed after one run of Lignite-Standard.

Table 6. Ash results

Run	Identification	Mean, %	SD, %	CV, %
1, 5, 6, 13, 18, 19, 25, 27	Lignite-Standard-1, 2, 3, 4, 6, 7, 8, 9	16.03	5.286	32.9
3, 8, 9, 15, 23, 24, 29, 30	Lignite-Modified50%-1, 2, 3, 4, 6, 7, 8, 9	34.81	9.058	26.0
32 ^a	DI water-Modified-5	92.34	NA ^b	NA
34 ^c	DI water-Standard-1	64.68	NA	NA

^a Completed after three consecutive runs of Lignite-Modified50%.

^b NA = Not available.

^c Completed after one run of Lignite-Standard.

Table 7. Na and Cl results

Run	Identification	Na, mg/L	Cl, mg/L
31 ^a	Lignite-Modified50%-10	11.2	43.7
33 ^b	Lignite-Standard-10	1.9	14.6

^a Completed after two consecutive runs of Lignite-Modified50%.

^b Completed after one run of DI Water-Modified 50%.

modified method reduced it by 8.5 h. The use of the modified method saved 8.25 h of total analytical time over the standard method (*see* Table 8).

Discussion

Run 21 (Blank-Modified 50%-2) was completed after Run 20 (Blank-Modified50%-1). This meant that DAX-8 should have been clean from any organic components prior to Run 21, other than acetone, which was used as the desorbing agent, as shown in the FTIR spectra. The nonidentifiable (blank) FTIR spectra for Run 21 indicated that acetone did not interfere with any spectral interpretations. Run 17 (Lignite-Standard-5) and Run 22 (Lignite-Modified50%-5) produced almost identical amounts of HFA, as expected, because both contained the same sample. Interestingly, both runs also showed some amounts of HN. This suggested that when using the standard method, both HFA and HN components were adsorbed by DAX-8 and desorbed using NaOH, which was later quantified as HFA.

Because of the use of acetone, the modified method resulted in more HN being detected. This agrees with the fact that acetone would desorb all organic components including HFA and HN, which were later quantified as HFA. This indicated that organic components being quantified by both standard and modified methods were actually a combination of mainly HFA and some HN, which still met the definition of HFA as “components soluble in both alkali and acids solutions, and adsorbed to a hydrophobic resin (DAX-8) at pH 1” (2).

Most interestingly, Run 26 (DI water-Modified50%-3), which was completed after Run 25 (Lignite-Standard-8), showed some amounts of HFA and HN. This suggests that DAX-8 adsorbed both of them, and the fact that it also contained HFA shows that regeneration steps using the standard method (two columns of DI water, one column of 0.1 HCl, and one column of DI water) completed on the previous run (Run 25) were inadequate.

Using the gravimetric method, HFA results obtained from both standard and modified methods showed that acetone at 50% strength was the right strength to produce results corresponding to those of the standard method using 0.1 M NaOH. Acetone at 25% strength produced lower results, suggesting that the desorption of HFA (and some HN) from DAX-8 was not complete. Acetone at 75% strength produced higher results, suggesting that more HN was desorbed from the resin. As shown earlier by the FTIR analysis, HFA results obtained from both standard and modified methods contained some amounts of HN. This indicated that, in terms of principles, the modified method did not deviate from the standard method, although its accuracy depended on the right strength of acetone being applied.

Table 8. Analytical times

Analytical step	Analytical time, h ^a		Modified method over standard method
	Standard method	Modified method	
Sample drying alkaline extraction, acidification, centrifuging, settling, FF through DAX-8 (adsorption) desorption	28	28	No difference
DAX-8 regeneration	0.5	0.75	Addition of acetone
IR-120 usage, regeneration	1.5	0	IR-120 not required
Rotovap usage, drying, ash corrections	27	20	Rotovap not required
Total analytical time	57	48.75	8.25 h shorter

^a Average of 28 runs to the closest 0.25 h.

For the modified method, implementing acetone at 50% strength within regeneration steps of DAX-8 (Runs 20–24, 26, and 28–32) or not implementing it (Runs 2–4, 7–12, and 14–16) did not have any effects on HFA results. This suggests that 50% acetone used during desorption earlier, together with two columns of DI water, one column of 0.1 M HCl, and one column of DI water during the regeneration afterwards, provided an adequate regeneration for the resin.

Run 20 (DI water-Modified50%-1, completed after three consecutive runs of the lignite sample using the standard method) quantified some organic components at 0.35%. These were leftover HN (and, most likely, some HFA; see the FTIR analysis above) originating from the three previous runs. For each run, it could be approximated at $0.35\% \div 3 = 0.12\%$. The same explanation applied for Run 28 (DI water-Modified50%-4, completed after one run of the lignite sample using the standard method), in which 0.16% of organic components were leftover HN (and some HFA) originating from the previous run. The fact that it also contained some HFA indicates that regeneration steps using the standard method completed on the previous runs (Runs 17–19 and 27) were inadequate.

Run 32 (DI water-Modified50%-5, completed after three consecutive runs of the lignite sample using the modified method at 50% strength) quantified very few organic components at 0.03%. These were leftover HN originating from the three previous runs. For each run, it could be approximated at $0.03\% \div 3 = 0.01\%$. This suggested that the modified method, because of the presence of acetone, provided an adequate (almost complete) regeneration on each of these three previous runs.

Run 34 (DI water-Standard-1, completed after one run of the lignite sample using the standard method) quantified some organic components at 0.31%. These were leftover HFA (and, most likely, some HN; see the FTIR analysis above) originating from the previous run. This suggests that DAX-8 adsorbed both HFA and HN. The fact that it also contained HFA indicates that regeneration steps using the standard method on the previous run were inadequate.

The gravimetric analysis found that the omission of IR-120 resulted in higher ash, as shown in Runs 3, 8, 9, 15, 23, 24, 29, and 30 (the modified method at 50% acetone strength, mean = 34.81%) in comparison to Runs 1, 5, 6, 13, 18, 19, 25, and 27 (the standard method, mean = 16.03%). However, these higher ash contents did not affect the accuracy of HFA quantification, as shown by the fact that results from both methods corresponded very well.

The gravimetric analysis for blank samples showed that Run 32 (Blank-Modified50%-5, completed after three consecutive runs of the lignite sample using the modified method at 50%

acetone strength) produced 92.34% ash. For each run, it could be approximated at $92.34\% \div 3 = 30.78\%$, which was smaller than 64.68% obtained from Run 34 (DI-water-Standard-1, completed after one run of the lignite sample using the standard method). These results corresponded well with the previous results. The modified method provided a much better DAX-8 regeneration, that Run 32 produced smaller organic components (HFA and HN) and ash contents leftover from the previous runs compared with those of Run 34.

The ionic analysis using ICP for Run 31 (Lignite-Modified 50%-10, completed after two consecutive runs of the lignite sample using the modified method at 50% strength acetone) produced 11.2 and 43.7 mg/L Na and Cl, respectively. For each run, it could be approximated at $11.2 \div 3 = 3.7$ and $43.7 \div 3 = 14.6$ mg/L, respectively (*Note*: Because it contained lignite material, Run 31 was included in this calculation). Run 33 (Lignite Standard-10, completed after one run of DI-water using the modified method at 50% acetone strength) produced lower results at 1.9 and 14.6 mg/L, respectively. This was in agreement with the previous findings that the omission of IR-120 resulted in higher ash contents.

It could be speculated that the use of the standard method would result in some HFA and HN being retained within DAX-8 after its regeneration, which would reach their maximum amounts and not increase after one run or so. When using fresh DAX-8, the first result could be expected to be lower, which would be followed by higher and stable results afterward. A similar situation, but at a smaller magnitude because of a better regeneration performance on DAX-8, could also be expected for the modified method.

The use of acetone as a desorbing agent reduced the total analytical time by 8.25 h. This represented approximately 14% time saving of the analytical time compared with the standard method.

Conclusions and Recommendations

Both standard and modified methods resulted in the presence of HN within the gravimetric quantification of HFA, in which more HN were detected using the modified method. This indicated that the organic components being quantified were actually a combination of mainly HFA and some HN, which still met the definition of HFA as “components soluble in both alkali and acids solutions, and adsorbed to a hydrophobic resin (DAX-8) at pH 1.”

The modified method using acetone at 50% strength produced HFA results that corresponded well with those of

the standard method using NaOH at 0.1 M. This method resulted in higher ash contents within the analytical solution, but they did not affect its accuracy. The modified method provided an adequate (almost complete) DAX-8 regeneration, but the standard method did not. This method required a significantly shorter analytical time because of the omission of IR-120 and a Rotovap.

This study demonstrated the potential of acetone as a desorbing agent for DAX-8 in the gravimetric quantification of HFA in lignite material. A detailed evaluation of the nature of the organic components being quantified (i.e., HFA and/or HN) using Nuclear Magnetic Resonance (NMR) analysis is recommended. A thorough evaluation of the capacity of DAX-8, involving larger volumes of resin, higher strengths of HFA in the evaluated sample, and various methods of regeneration (including the use of acetone at a higher strength for both standard and modified methods), is also recommended.

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