

Colorimetric Determination of Aluminum in Sodium Diacetate Using Hematoxylin

Y. Yildiz*

Complete Analysis Laboratories, Analytical Chemistry Research Department. 810 N 2nd Avenue, Highland Park, New Jersey 08904-USA

O. Anderson Bediako

Rutgers University School of Environmental and Biological Sciences, New Brunswick, New Jersey 08901-USA

Abstract

Here we are reporting determination of metallic aluminum in sodium diacetate colorimetrically by the use of hematoxylin. Many sophisticated techniques such as pulse polarography, HPLC, AAS, ICP-AES, ICP-MS, are available for the determination of aluminum at trace levels in complex materials are known. Atomic Absorption Spectrophotometer was used to determine aluminum (Al) at 0.1 mg/kg level present in sodium diacetate NaH(OAc)₂. So we propose determination of aluminum by Hematoxylin, with formation of lake at pH 4.5 and measurement of the unstable color at 540 nm.

Keywords: Sodium diacetate; Aluminum; Spectrophotometric determination; Hematoxylin.



CC BY: [Creative Commons Attribution License 4.0](https://creativecommons.org/licenses/by/4.0/)

1. Introduction

High amounts of aluminum are toxic for human beings [1]. However, its micro nutrient role is well recognized. Aluminum can cause neurotoxicity in very high doses which can alter the function of blood brain barrier [2]. Aluminum increases estrogen related gene expression in human breast cancer cells grown in the laboratory [3]. Hence, accurate determination of aluminum in trace quantities in various natural systems is very important. Spectrophotometry is a good trace analysis technique. Recently several spectroscopic methods [4-29] based on the use of various organic reagents are reported for the determination of aluminum [1].

Sodium diacetate is a molecular compound of acetic acid, sodium acetate and water of hydration. It is a salt of acetic acid with formula NaH(C₂H₃O₂)₂. Also described as the sodium salt of hydrogen-bonded anion (CH₃CO₂)⁻ H⁺. [30, 31]. The technical grade is prepared synthetically by reacting sodium carbonate with acetic acid. Special grades are produced by reacting anhydrous sodium acetate and acetic acid. Structural formula has been shown in Figure 1. A physical and chemical property of sodium diacetate is shown in Table 1.[2, 3, 30, 32, 33].

The ingredient is used as a food additive, and as an antimicrobial agent. It has E number E₂₆₂ and is used to impart a salt and vinegar flavor [1].

Hematoxylin is a natural organic dye compound extracted with ether from the heartwood of the logwood tree (Hematoxylin campechianum). It is also called Hematoxiline, Hydroxybrazilin; and Natural Black I. A yellow or red crystalline compound; acidic, melting point 100 °C (212 °F), soluble in hot water, partially soluble in methanol, very slightly soluble in diethyl ether. Its empirical formula is C₁₆H₄)₆. xH₂O. Hematoxylin is used as a histologic stain and also as an indicator. Its structure is shown in Figure 2.

Table-1. Physical and chemical properties of sodium diacetate

Chemical name, Synonyms	Sodium hydrogen diacetate; Sodium acid acetate; Acetate buffer; Monosodium diacetate; Acetate sodium acetate
Molecular formula:	C ₄ H ₆ NaO ₄ ⁻
Appearance (Physical state, color):	White, clear colorless, hygroscopic crystalline powder with the odor of acetic acid.
Molecular weight:	142.09 g mol ⁻¹
Density:	1.5285 g/cm ³
Usage	Antimicrobial agent in bakery and foodstuffs, flavor enhancer.
Melting point	323-329 °C
Flash point	40°C (104°F)
pH	4.5 - 5.0 (1 in 10 solution)
Decomposition	When heated to decomposition it emits acrid smoke and irritating fumes.
Solubility:	Slightly soluble in alcohol; insoluble in ether; freely soluble in water

Figure-1. Structure of sodium acetate

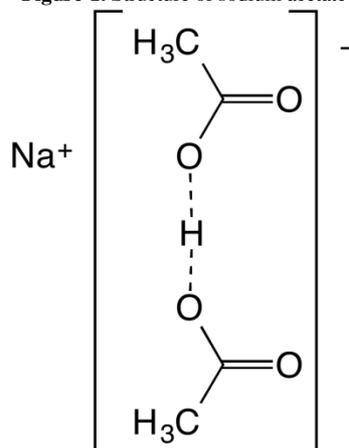
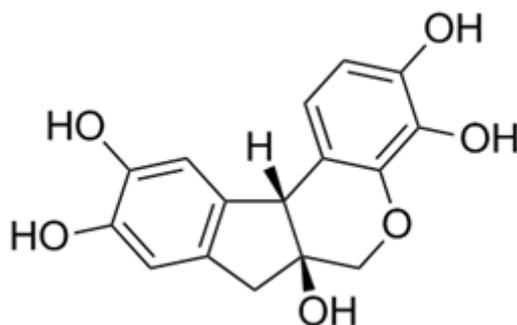


Figure-2. Hematoxylin Chemical Structure



2. Materials and Method

2.1. Instrumentation

UV/Visible spectrophotometers are widely used by many laboratories including those in academia and research as well as industrial quality assurance. The technique is mainly used quantitatively. The absorbance spectra for all measurements were carried out using a Shimadzu 1601 PC double beam UV-VIS Spectrophotometer, with 1 cm quartz cells and 2.0 nm fixed slit width. The spectrophotometer was connected to a computer, loaded with Shimadzu UVPC software, and equipped with an Epson LQ-850 printer.1 [34].

2.2. Equipment

- DI water wash bottle
- Spatula
- Large disposable pipette
- Thin disposable pipettes (marked for 1 mL)
- 5 mL volumetric pipet
- 10-100 μ L micropipettes with yellow tips
- Small magnetic stir bar and stirrer
- pH meter
- 25 mL graduated cylinder

2.3. Reagents and Solutions

All the chemicals used were of analytical reagent grade of the highest purity available.

- High -purity de-ionized water was obtained by Aries High Purity Water System, Aries Filter Works. The aluminum level in the high-purity de-ionized water was found to be below the spectrophotometric detection limit (3s of the blank) of 1 μ g/L. Glass vessels were cleaned by soaking in acidified solution of $K_2Cr_2O_7$ followed by washing with concentrated HNO_3 and rinsed several times with high purity deionized water.
- Concentrated aluminum Standard Stock Solution: 20 mg/L Aluminum Stock Standard Solution with 3% HNO_3 (v/v). Working standard solutions were prepared after suitable dilutions of the stock solution with redistilled deionized water.
- Hematoxylin solution: Dissolve approximately 5 mg in 40 mL 95% ethyl alcohol, add one drop of hydrochloric acid, and dilute to 50 mL with 95% ethyl alcohol. (no older than 2 hours). Obtained from Roche Diagnostics.
- Synthetic $NaH(OAc)_2$: eg 12.5 g $NaOAc$ +12.5 g $HOAc$ per 200 mL
- 1:1 hydrochloric acid
- KOH pellets, KOH (aq) approximately 5 pellets per 50 mL H_2O .

- 25 % (NH₄)₂CO₃, prepare with stirring and heating
- 2% Starch, prepare with stirring and heating

2.4. General Procedure

1.25 g sodium diacetate was weighed in 50 mL beaker. 2 mL 1:1 HCl (6N) was added to convert Al to Al³⁺ with stir magnetically. 8 mL H₂O and KOH pellets were added to about pH=6.0. For the pH adjustment, a 1.0 mL 2% starch solution and 1 mL 25% (NH₄) CO₃ have been added. Adjusted pH was 8.3 or slightly less. 5 mL of hematoxylin solution was added by pipet. The contents of beaker were poured to 25 mL volumetric flask and the beaker rinsed into the volumetric flask and the mixture was diluted up to the 25 mL with deionized water. The absorbance was measured at 650 nm each time. Also measured absorbance at 650 nm for 10 mL synthetic NaH(OAc)₂ treated similarly, this was blank. The deionized water was measured at 650 nm, for the background.

2.5. Spectrophotometric Curves

The spectrophotometric curves obtained for the standards and for the blank are shown in Table 1, and Table 2. Sodium diacetate was used as the blank. Since a faint red color is produced by the reaction of aluminum and hematoxylin in slightly acid solution, and requires up to 40 minutes for full color development.

3. Results and Discussion

The direct method was applied for the determination of aluminum in sodium diacetate by hematoxylin. Studies had shown that the Hematoxylin could react with aluminum ion (Al³⁺) to form colored complexes that could be monitored spectrophotometrically. The color was stable for two hours.

Table-2. Absorbance of Al Standards

Standard Concentration (mg/L)	DF	Absorbance	Blank-corrected Absorbance
Air		0.0000	
Water	1	0.0000	
Blank	1	0.0006	
2.0	1	0.0128	0.0122
5.0	1	0.0304	0.0298
10.0	1	0.0597	0.0591
20.0	1	0.1184	0.1178

Table 1. Raw data, absorbance of Aluminum standard solutions, and the blank-corrected absorbance calculated using Equation (1).

Table-3. Calibration Curve Data

[Al] (mg/L)	Abs	Slope	0.0059
0.00	0.0006	Intercept	0.0005
2.0	0.0122	R ²	1.0000
5.0	0.0298		
10.0	0.0591		
20.0	0.1178		

Table 2. Data used to plot the calibration curve graph, [Al] concentration and blank-corrected absorbance; slope, intercept, and R² values for the line of best fit.

Figure3. Calibration curve, linear plot of [Al] concentration against blank-corrected absorbance at 650 nm.

Figure-3. Calibration curve

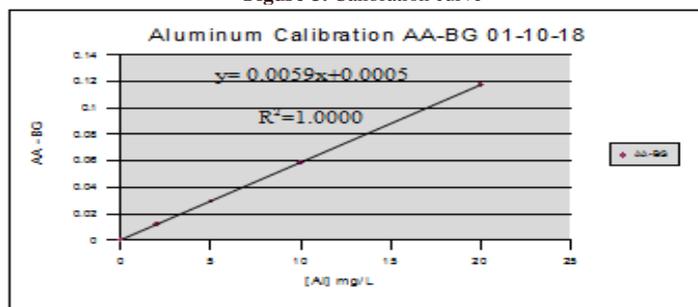


Table-4. Absorbance of Sodium Diacetate Samples

Sample	DF	Absorbance	Blank-corrected Absorbance	[Al] (mg/L)	Sample weight (g)	Final volume (mL)	[Al] (mg/kg)
Air	1	0.0000					
Water	1	0.0000					
Blank	1	0.0006					
10 ppm Check Std	1	0.0596	0.0590	9.98			
Sample	1	0.0012	0.0006	0.01	1.2500	25.0	0.28
Sample dup	1	0.0012	0.0006	0.01	1.2500	25.0	0.28
Spiked Sample	1	0.0014	0.0008	0.08	1.2500	25.0	0.96
Spiked Sample dup	1	0.0014	0.0008	0.08	1.2500	25.0	0.96

Table 3 Data of absorbance of sample solutions and spiked sample solutions, each analyzed in duplicate; concentration of Al calculated using Equations (2) and (3).

Equation (1): Blank-corrected absorbance = Observed absorbance – Blank absorbance.

Equation (2): [Al] (mg/L) = (Blank-corrected Absorbance – 0.0059) / 0.0005

Equation (3): [Al] (mg/kg) = [Al] (mg/L) * Final volume (mL) / Sample weight (g)

4. Conclusion

UV-VIS Spectrophotometric determination of aluminum in disodium acetate with hematoxylin was found to be adequately sensitive in terms of linearity, repeatability, and accuracy. The determination of correlation coefficient (R^2) was found to be 1.0000. Concentration of spiking solution: 100 mg/L, spiking solution: 0.1875 mL, sample volume: 25 mL, spiked amount: 0.75 mg/L, true value: 0.01875 mg. Average percent matrix spike recovery (%R) was 90.7 %, and relative percentage difference (%RPD) was 0.00%. The percent recovery was found to be 90.66% for spiked sample, and 90.66% for the duplicate spiked sample. The results were within the specification of 0.1 mg/Kg maximum, with the average concentration of Al in sample found to be 0.28 mg/Kg.

Acknowledgment

We would like to thank you to Professor Gregory Edens, Bloomfield College of new Jersey for his valuable information to parts of this paper.

References

- [1] 21 CFR 184.1754; "U.S. National archives and records administration's electronic code of federal regulations." 2006. Available: <http://www.ecfr.gov>
- [2] O'Neil, M. J., 2001. *The merck index - An encyclopedia of chemicals, Drugs, and biologicals*. 13th ed. Whitehouse Station, NJ: Merck and Co., Inc. p. 1539.
- [3] Lewis, R. J. S., 2001. *Hawley's condensed chemical dictionary*. New York, NY: John Wiley & Sons, Inc. p. 1010.
- [4] Kamino, S., Yamaguchi, T., Mori, T., Miyamoto, M., Kusumi, Y., and Fujita, Y., 2005. "Spectrophotometric determination of aluminum with m-Carboxyphenylfluorone, a Novel chemical probe and its application." *Anal Sci.*, vol. 21, p. 1549.
- [5] Zhou, N., 2004. "Selective spectrophotometric determination of aluminium in the presence of beryllium and lanthanide cations." *Microchimica Acta*, vol. 146, p. 73.
- [6] Idriss, K. A., Hashem, E. Y., Aziz, M. S. A., and Ahmed, H. M., 2000. "Direct spectrophotometric determination of aluminum oxide in Portland cement and cement clinker. An insight into the solution equilibria and analytical aspects of the aluminum–quinizarin system." *Analyst*, vol. 125, p. 221.
- [7] Zareba, S. and Melke, J., 2000. "Spectrophotometric determination of aluminum in pharmaceutical preparations by azo dyes of 1,2,4- triazole series." *Pharm Acta Helv.*,
- [8] Tufan, G., Dilek, U. U., Tevfik, G., and Ali, H., 2005. "2,2',3,4-Tetrahydroxy-3'-sulpho-5'-nitroazobenzene for spectrophotometric determination of aluminum in pharmaceutical suspensions and granite." *Anal Chimica Acta*, vol. 545, p. 107.
- [9] Spinola, A., 1998. "Spectrophotometric determination of aluminum in iron ores using solid-phase extraction." *J. Braz. Chem. Soc.*, vol. 9, p. 151.
- [10] Bahrama, M., Madrakianb, T., Bozorgzadehb, T., and Afkhamib, A., 2007. "Micellemediated extraction for simultaneous spectrophotometric determination of aluminum and beryllium using mean centering of ratio spectra." *Talanta*, vol. 72, p. 408.
- [11] Shokrollahi, M., Ghaedi, N. M. S., and Rajabi, H. R., 2008. "Selective and sensitive spectrophotometric method for determination of sub-micro-molar amounts of aluminum ion." *J. Haza Mate*, vol. 151, p. 642.
- [12] Niazi, A., Zolgharnein, J., and Davoodabadi, M. R., 2007. "Simultaneous determination of aluminum and iron with hematoxylin using spectrophotometric and orthogonal signal correction-partial least squares in plant and water." *Ann. Chim.*, vol. 97, p. 1181.

- [13] Zheng, H. L., Xiong, M. G., Gong, Y. K., Peng, D. J., and Li, L. C., 2007. "Catalytic spectrophotometric determination of trace aluminum with indigo carmine." *Spectrochim Acta A Mol Biomol Spectrosc*, vol. 66, p. 1243.
- [14] Carpani, I., Scavetta, E., and Tonelli, D., 2004. "Spectrophotometric determination of aluminum and nickel." *Ann. Chim.*, vol. 94, p. 365.
- [15] He, R. and Wang, J., 2000. "Novel catalytic spectrophotometric procedure for the Determination of trace-level aluminum." *Anal. Chimica Acta.*, vol. 412, p. 241.
- [16] Pourreza, N. and Behpour, M., 1999. "Column preconcentration of aluminum using Eriochrome Cyanine R and methyltriethylammonium chloride adsorbent supported on naphthalene with subsequent spectrophotometric determination." *Microchemical J.*, vol. 63, p. 250.
- [17] Afkhani, A. and Zarei, A. R., 2004. "Simultaneous kinetic determination of beryllium and aluminum by spectrophotometric H-point standard addition method." *Anal Sci.*, vol. 20, p. 1711.
- [18] Rizk, M., Zakhari, N. R., Toubar, S. S., and El-Shabrawy, Y., 1995. "Spectrophotometric determination of aluminum and copper ions using spadns." *Microchimica Acta*, vol. 118, p. 239.
- [19] Buratti, M., Valla, C., Pellegrino, O., Rubino, F. M., and Colombi, A., 2006. "Aluminum determination in biological fluids and dialysis concentration via chelation with 8-hydroxy quinolin and solvent extraction fluorimetry." *Anal Biochem*, vol. 353, p. 63.
- [20] Ahmed, M. J. and Hossan, J., 1995. "Spectrophotometric determination of aluminum by morin." *Talanta*, vol. 42, p. 1135.
- [21] Diaz, A. M., Mariscal, J. M. H., Reguera, M. I. P., and Vallvey, L. F. C., 1993. "Determination of trace of aluminum with chrome azurol S by solid-phase spectrophotometry." *Talanta*, vol. 40, p. 1059.
- [22] Agnihotri, N. K., Singh, H. B., Sharma, R. L., and Singh, V. K., 1993. "Simultaneous determination of beryllium and aluminum in mixtures using derivative spectrophotometry." *Talanta*, vol. 40, p. 415.
- [23] Ying-ping, H., Ke-mei, Y., and Hua-shan, Z., 1999. "Spectrophotometric determination of aluminum with 2,3,7-trihydroxy-9-[4-(2,4-dihydroxy)phenylazo] phenylfluorone." *Wuhan University J. Natural Sci.*, vol. 4, p. 219.
- [24] Mendez, J. H., Martinez, R. C., Cordero, B. M., and Davila, L. G., 1983. "Spectrophotometric determination of aluminum with alizarin red S Direct Spectrophotometric determination of Aluminum (III) using 5-Bromo-2-hydroxy-3-10 | Page sensitized with polyvinylpyrrolidone." *SAlytica Chimica Acta*, vol. 149, p. 379. Available: www.iosrjournals.org
- [25] Luo, M. and Bi, S., 2003. "Solid phase extraction spectrophotometric determination of dissolved aluminum in soil extracts and ground waters." *J. Inorg Biochem*, vol. 97, p. 173.
- [26] Valencia, M. C., Boudra, S., and Bosque-Sendra, J. M., 1996. "Simultaneous determination of aluminum and beryllium at the subnanogram per millilitre level by solid-phase derivative spectrophotometry." *Anal Chimica Acta*, vol. 327, p. 73.
- [27] Azhari, S. J. and Amin, S. A., 2007. "Highly sensitive and highly selective spectrophotometric determination of aluminum after collection on a membrane filter using 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo) quinoxaline and zephiramine." *Anal Letters*, vol. 40, p. 2959.
- [28] Saritha, B. and Sreenivasulu, R. T., 2014. "Direct Spectrophotometric determination of Al (III) using 5-Bromo-2-hydroxy-3-methoxybenzaldehyde-P-hydroxybenzoic hydrazine." *Journal of Applied Chemistry*, vol. 7, pp. 05-10.
- [29] Ahmed, M. J. and Nasiruddin, M., 2007. "A simple spectrophotometric method for the determination of cobalt in industrial, environmental, biological and Soil samples using bis(salicylaldehyde)orthophenylenediamine." *Chemosphere*, vol. 67, p. 2020.
- [30] Barrow, M. J., Currie, M., Muir, K. W., Speakman, J. C., and White, D. N. J., 1975. "Crystal structures of some acid salts of monobasic acids. XVII. Structure of sodium hydrogen diacetate, redetermined by neutron diffraction." *Journal of the Chemical Society, Perkin Transactions 2: Physical Organic Chemistry*, pp. 15-18.
- [31] Peter, J., 2010. "Taormina "Implications of salt and sodium reduction on microbial food safety." *Critical Reviews in Food Science and Nutrition*, vol. 50, pp. 209-227.
- [32] Furia, T. E., 1972. *CRC handbook of food additives*. 2nd ed. Cleveland: The Chemical Rubber Co. p. 148.
- [33] Lewis, R. J. S., 2004. *Sax's dangerous properties of industrial materials*. 11th ed. Hoboken, NJ: Wiley-Interscience, Wiley & Sons, Inc.
- [34] Yildiz, Y., Jan, A., Pendyala, L., and Yildiz, B., 2007. "Determination of tin in trityl candesartan by uv-vis spectrophotometer using phenylfluorone." *World Journal of Applied Chemistry*, vol. 2, pp. 134-139.