Investigations on Wastewater Pollutants Using Derivative Spectroscopy

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Using two examples (uric acid determination in municipal wastewaters and nitrate/nitrite determination in less organic polluted surface or ground waters) some advantages of derivative spectroscopy in the UV/VIS-range for the quantitative evaluation of water pollution loads are demonstrated. By careful observing and avoiding matrix effects derivative spectroscopy can be applied directly to the analysis of sample constituents with a minimum of preparation and separation expenditure compared to standard methods.

1. INTRODUCTION

Recent developments in spectrophotometer design such as signal processing by microprocessors or other highly integrated electronic devices and enhanced methods for wavelength modulation, make it possible to generate directly and in a simple manner more precise and detailed information on the UV/VIS absorption characteristics of aqueous solutions applying derivatives of zero-order spectra. Derivative spectroscopy in the UV/VIS range may get increasingly more used—not only for magnifying fine structures of spectral curves but also for direct concentration measurements. Derivative spectroscopy means that higher order derivatives (first, second and higher) are calculated or generated from absorption spectra with respect to frequency.

The techniques applied are summarized in Refs. [1–7] and semi-quantitative understandings of the general effects observed in actual derivative spectra are given in Refs. [8–12].

Besides a reduced signal to noise ratio, in practical applications some advantages of derivative spectroscopy may be: enhancement of spectral structure; partial removal of unspecific background absorption due to light scattering effects; partial or total elimination of less detailed background absorption from broad and low intensity peaks.

Due to these characteristics derivate spectroscopy may be looked upon as a powerful technique, in particular for the analysis of organic-biological wastewater pollution loads in the sense of direct measurements with little or no sample preparation, compound separation or enrichment procedures. This is of special importance when a large number of samples has to be measured in a short time; besides, since the sample is not destroyed or substantially changed, low sample volumes can be analysed under different aspects.

It is the aim of this paper to show some possibilities of derivative spectroscopy for wastewater, surface or groundwater pollution using two practical applications (uric acid in municipal wastewater discharges and nitrate/nitrite leachates from different sources).

2. MATERIALS AND METHODS

Derivative spectra and enzymatic investigations were recorded on a Perkin Elmer Model 554 UV/VIS spectrophotometer. Chemicals used were at least of reagent grade (p.A.) from Merck (Darmstadt, W. Germany) and Boehringer, (Mannheim, W. Germany). pH measurements were performed with a combination glass electrode (Ingold, Frankfurt, W. Germany) connected with a Knick Model 645 pH-meter (Berlin, W. Germany). For electrode calibrations commercial buffer solutions (Merck) were used.

3. RESULTS AND DISCUSSION

Uric acid in municipal wastewater discharges

Municipal wastewater carries high organic-biological pollution loads most of which are biodegradable. As an integral measure for the amount of load and the aerobic digestion the BOD_5 (biochemical oxygen demand within five days) is used. Measuring this value is time consuming and because of various reasons values obtained may not always be reliable.[13] This is why the BOD-value cannot be used as a measure for on-line regulating the purifying conditions of a sewage treatment plant, although the BOD would fit best the parameter needed. Generally the operation conditions of a sewage plant are maintained indirectly by controlling the oxygen consumption in the aeration tank without knowing

the real amount of organic load to be handled. In addition for the secondary effluents—the discharges from the final settlement tank of a sewage plant it—it is difficult or even impossible to record continuously by any parameter the overall purifying performance of the plant. Therefore we carried out a systematic investigation on organic-biological compounds in general present in municipal wastewaters to correlate these with BOD-values.

One of these compounds was uric acid which is present in municipal wastewaters originating from human urine at levels of about 250–750 mg/person and day.[14]

The determination method for uric acid had to meet the following conditions: quick handling of large numbers of samples (with the possibility of continuous and automated measurement); direct measurement (with a minimum of sample preparation); accuracy at least comparable to that of standard methods; applicability as widely as possible for wastewater mixtures (municipal and industrial).

The uric acid determination in wastewaters by derivative spectroscopy proved to be for this case a generally applicable method based on the above terms.

Figure 1 shows the normal and first-derivative spectrum of uric acid in distilled water. Calculations of uric acid concentrations from the derivative spectrum were performed using the values of the absorption difference between λ max $= 305$ nm and λ min $= 280$ nm at pH $= 12.0$. Calibration graphs as well as double standard addition were used.

Figure 2 displays typical spectra obtained from municipal wastewater discharges which were analyzed as described above. From Figure 2 the potential of derivative spectroscopy becomes evident since although there is a strong background absorption—resulting from a slight turbidity and probably a lot of minor additional constituents leading to low-intense, broad and overlapping peaks—the derivative spectrum of uric acid can clearly be identified and evaluated on carefully considering the absorbance linearity range of the spectrophotometer used.

On addition of uricase the derivative spectrum of uric acid disappears, which in turn—because of the specific reaction of uricase—permits the identification of the uric acid spectrum for complex spectral features.

Although municipal wastewater may vary in composition and consists of a complex mixture of different organic, biological and inorganic constituents, no disturbances due to matrix effects for the uric acid determination by derivative spectroscopy have been observed so far.

Conditions for the experimental procedure and accuracy of the method are presented in detail elsewhere.[15] Table I briefly summarizes the results which were obtained from a comparison between the derivative
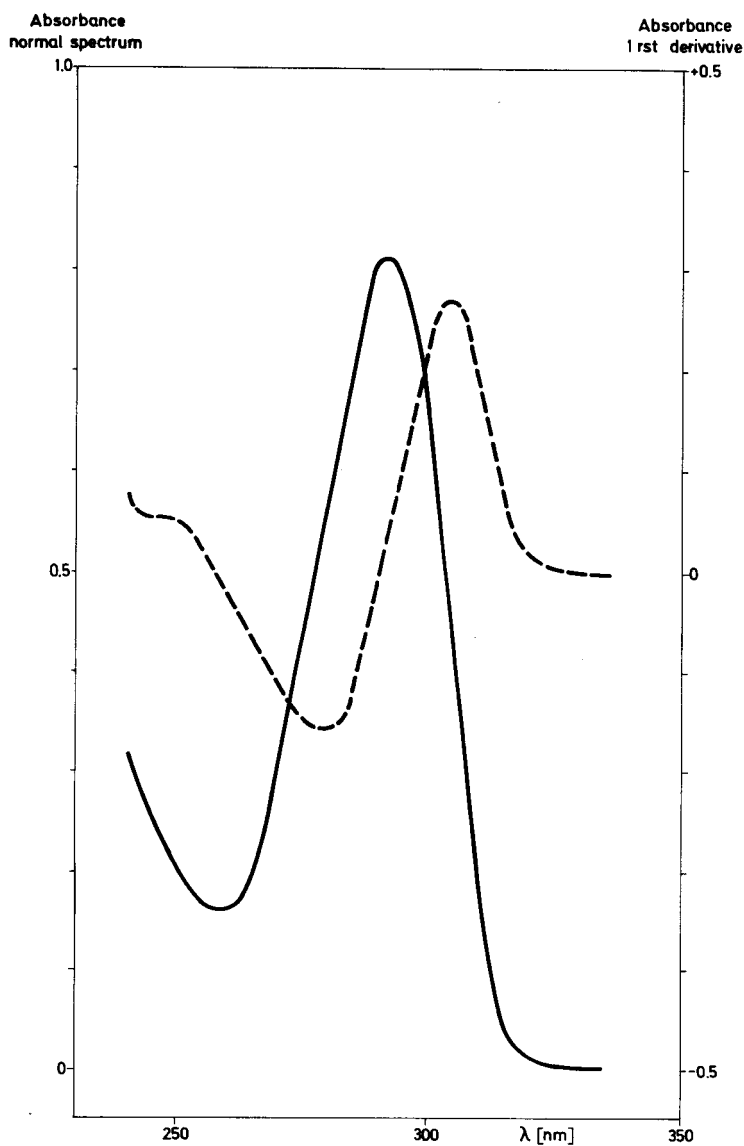
FIGURE 1 Normal (———) and first derivative (----) of the uric acid spectrum in distilled water; pH = 12.0; uric acid concentration: 10 mg/l; spectrophotometer conditions: 10 mm pathlength; filter factor 3; recording speed 120 nm/min; slid width 2.0 nm.
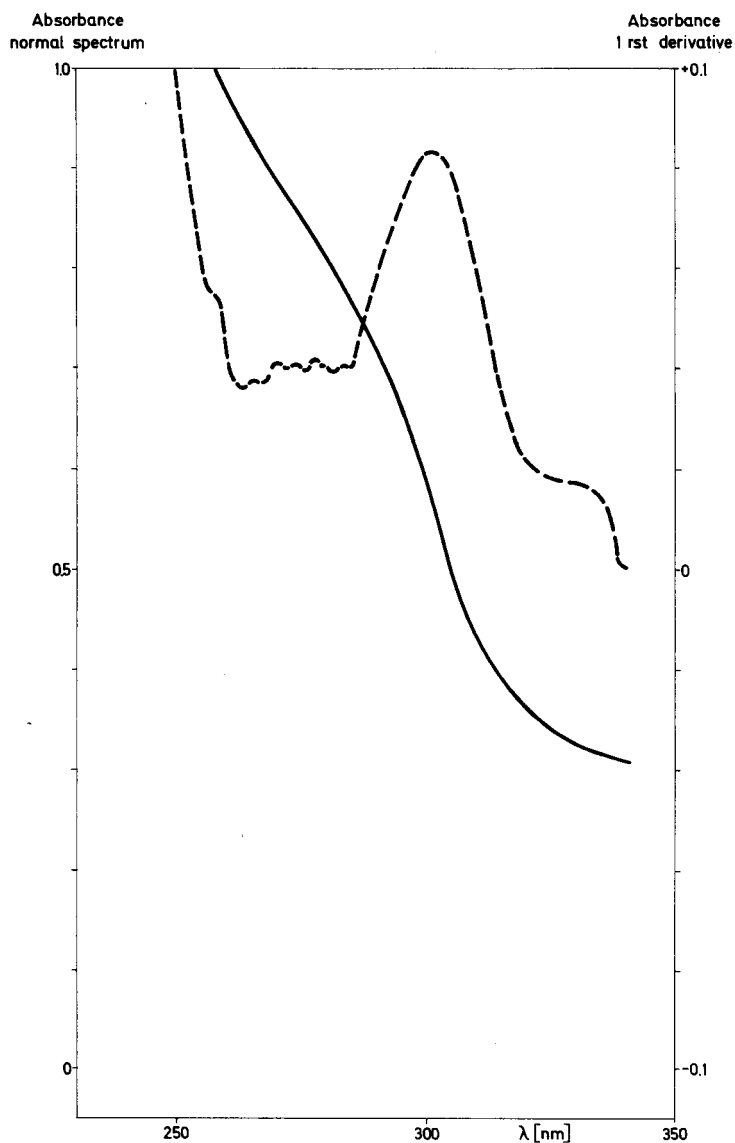
FIGURE 2 Normal (——) and first derivative spectrum (----) of a municipal wastewater sample (diluted 1:1 with distilled water; 1.25 mg uric acid/l; pH = 12.0); spectrophotometer conditions as Figure 1.

TABLE I

Comparison of accuracy and recovery for the uric acid determination by the enzymatic
uricase method and the described method using derivative spectroscopy

Sample	Number of samples	Uricase method mean standard deviation [%]	Derivative method mean standard deviation [%]	recovery [%][a]
Distilled water	6	0.5	0.9	103.0
Human urine	10	0.3	1.2	101.0
Municipal wastewater	20	4.5[b]	4.9	103.6

[a]with respect to values found with uricase method.
[b]values which could not be accurately detected because of inhibition reactions not included.

and enzymatic method (uricase reaction [16,17]) for different matrices
(pure water, human urine, municipal wastewater) revealing no significant
differences.

The application of the enzymatic uric acid determination in wastewater
is often limited, probably due to the inhibition by certain organic or
inorganic wastewater constituents. In addition this biochemical method—
although highly specific—is time consuming and expensive compared to
the method using derivative spectroscopy and thus may not meet the
routine and reliability conditions necessary in our application case. This
holds, too, for several other uric acid determination procedures reviewed
in Ref. [17].

As a result of the described rapid analysis technique for uric acid
systematic investigations of the uric acid content and the BOD_5 or COD
(chemical oxygen demand, measured by the dichromate method)[18]
values of influent wastewaters to a municipal sewage treatment plant
(about 40,000 population equivalents) could be performed. These
showed—under varying conditions (high and low inputs, day and night,
etc.)—that there may be a correlation between the amount of uric acid
and the COD expressed by a linear regression factor[19] of $r = 0.8$
(including all of about 100 measured values). For correlation, instead of
the BOD_5 the COD was chosen because of two reasons: firstly, the BOD_5
measurement in such a case takes too much time and laboratory capacity;
besides for municipal wastewaters a correlation between BOD_5 and COD
exists which can be set to about $BOD_5/COD = 0.6$[20] for the plant
under test.

Figure 3 displays as an example an averaged daytime course (five days)
for the total amount of uric acid present in the influent of a municipal
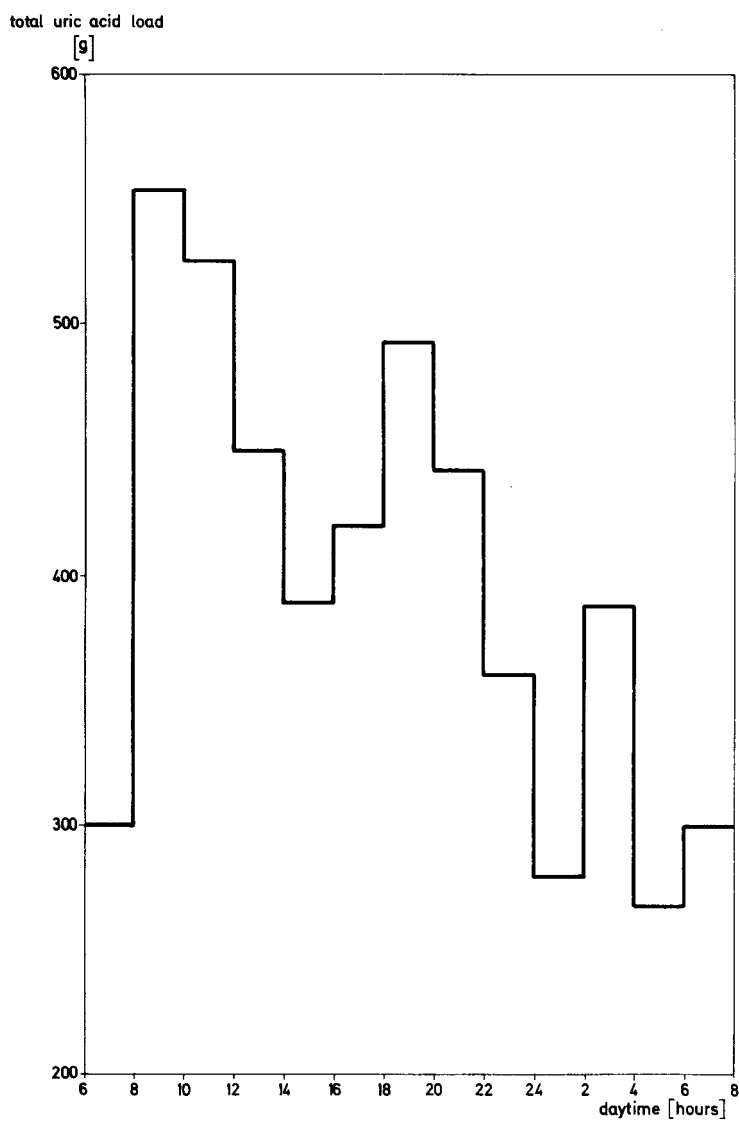sewage treatment plant.

FIGURE 3 Averaged daytime course (5 days) of the uric acid load of a municipal sewerage treatment plant.

Nitrate/nitrite determination by derivative spectroscopy

In surface and groundwater pollution, nitrate together with phosphate plays an important role in particular regarding eutrophication or anaerobic digestion reactions. In addition, drinking water standards demand control of nitrate due to health aspects.

For the direct determination of nitrate at low concentration levels its normal spectrum absorption peak at $\lambda = 210\,nm$ can be used. Because of strong interferences with organic or inorganic compounds different background corrections and sample-preparation procedures have been applied (reviewed in Ref. 21)

At high concentration levels a nitrate absorption peak with its maximum at $\lambda = 300\,nm$ becomes visible (see Figure 4). Unfortunately this peak is strongly overlapped by a nitrite peak with a maximum at $\lambda = 352\,nm$. A quantitative evaluation of nitrate/nitrite concentration in mixtures directly from the normal absorption spectra does not seem possible.

Figure 5 displays the corresponding first-order derivative spectra. As can be recognized the essential part of the nitrite derivative curve is well separated from that of nitrate. Thus the nitrite concentration can be evaluated directly and independently using the absorption difference of the first derivative between $\lambda\,max = 372\,nm$ and $\lambda\,min = 336\,nm$ (with some, although minor, distortion at $\lambda\,min = 336\,nm$) or preferably using the absorption difference between $\lambda\,max. = 372\,nm$ and the corresponding baseline at this wavelength.

The nitrate derivative curve (Figure 5) cannot be analyzed in the same way (absorption difference between $\lambda\,max = 318\,nm$ and $\lambda\,min = 282\,nm$). The corresponding nitrate concentration values differ from its actual size due to the distortion of the nitrate peak by nitrite present. Since the distortion effect (difference between nitrate measured and expected, $\Delta c_{nitrate}$) is proportional to the nitrite concentration present, it can be measured as a function of the nitrite concentration leading to a correction function:

$$\Delta c_{nitrate} = f(c_{nitrite}).$$

In practical applications the nitrite concentration has to be measured from its derivative curve as described above. After calculation of $\Delta c_{nitrate}$ the actual nitrate concentration can be evaluated too.

Table II summarizes some spectral and analytical data for the suggested simultaneous nitrate/nitrite determination method. Although the detection limits for nitrate and nitrite are relatively high (50 mg/l and 5 mg/l, respectively for 50-mm pathlength cells) the method may be very convenient for rapidly and directly controlling nitrate/nitrite levels of
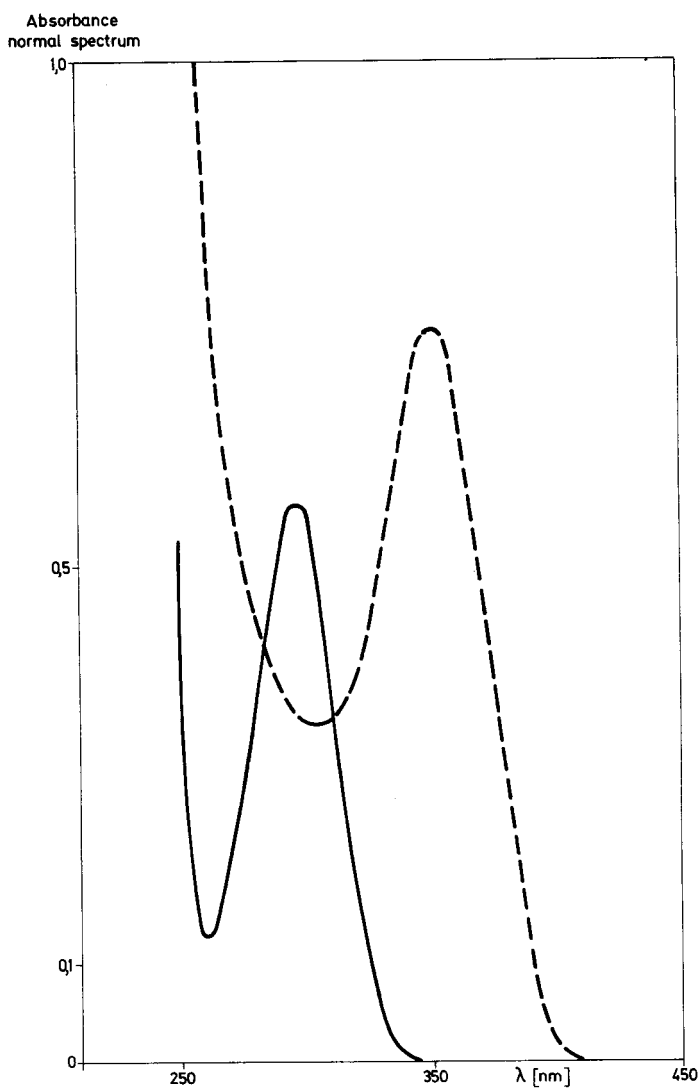
FIGURE 4 Normal absorption spectra of nitrate (——,1 g/l) and nitrite (---, 300 mg/l) in aqueous solution at neutral pH; 50 mm cuvettes; other spectral conditions as for Figure 1.
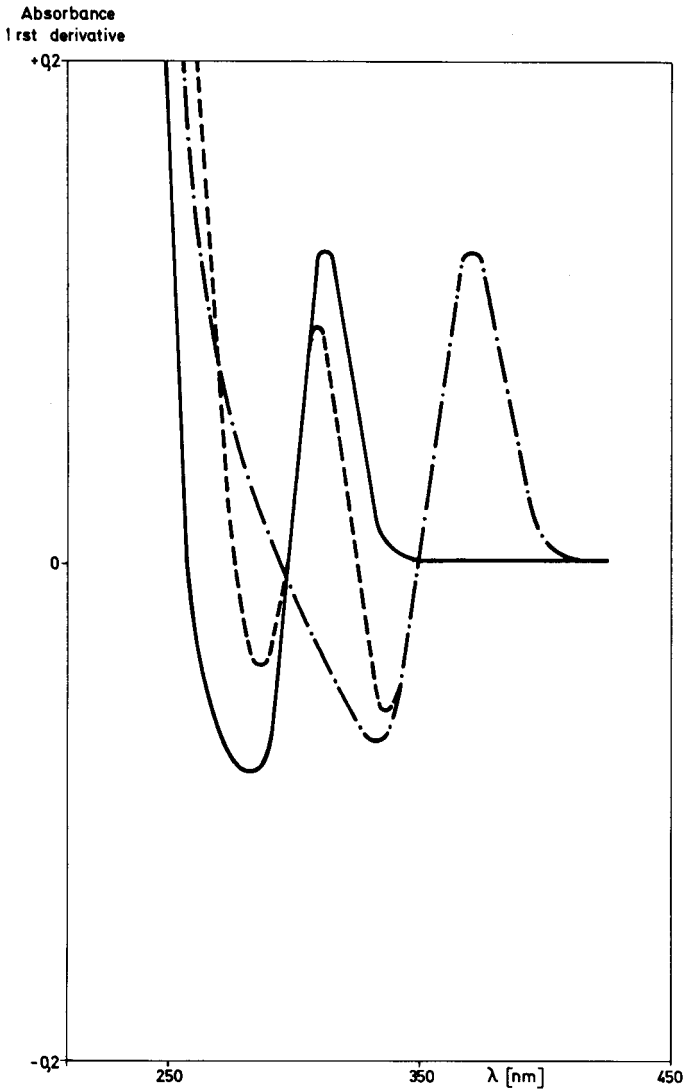
FIGURE 5   First derivative spectra of aqueous solutions of 1 g/l of nitrate (——), 300 mg/l of nitrite (— · — · —) and a mixture of the respective concentrations of nitrate/nitrite (---); spectrophotometer conditions as for Figure 4.

TABLE II

Summary of spectral parameters for the nitrate/nitrite determination from derivative spectra (first order)

Compound	Spectrum	λ max [nm]	λ max [nm]	λ min [nm]	$\Delta v_{1/2}$ [nm]	Application range [mg/l] (50 mm pathlength)
Nitrate	normal	300			40	
	first derivative		318	282		50–3000
Nitrite	normal	352			56	
	first derivative		372	336		5–400

natural waters (groundwater, surface water, drinking water). The technique also has a potential for the analysis of soil extracts and fertilizers.

It should be clearly stated that organic or inorganic sample constituents showing absorption peaks between 250 and 400 nm may cause severe difficulties when determining nitrate/nitrite by derivative spectroscopy. In such a case additional sample preparation procedures (precipitation reactions and/or chromatographic separation techniques similar to Ref. 21) have to be applied. As a general rule, using the suggested method, matrix effects always have to be checked out carefully. This is why no generalization of the method in terms of accuracy or recovery will be made here. If the above cited margins are correctly observed it is our experience that the accuracy is at least comparable to that of standard methods.

4. CONCLUSIONS

By applying derivative spectroscopy for the determination of uric acid in municipal wastewaters it can be shown that rapid and direct measurements with at least the same accuracy as in other methods are possible. Large numbers of samples can be easily handled. Sample preparation is minimized (adjustment of pH, partial removal of suspended solids by centrifuging). If necessary, measurements can be automated or performed "quasi" continuously using a flow-proportional batch system. This permits on-line detection of organic-biological pollution loads of municipal sewage treatment plants for controlling and maintaining optimum working performance with respect to the digestion of organic-biological pollution loads. In such a case a correlation between uric acid concentration and COD/BOD must given.

The advantages of derivative spectroscopy for the determination of high level nitrate/nitrite concentrations can be summarized in terms of a direct, rapid and simultaneous measurement of both parameters in less organic polluted waters. If problems arise, due to the presence of specific organic or inorganic sample constituents, an additional sample preparation procedure will have to be applied.

Acknowledgements

References

1. T. C. O'Haver, *Anal. Chem.* **51**, 91 A (1979).
2. W. L. Butler and D. W. Hopkins, *Photochem. and Photobiol.* **12**, 451 (1970).
3. G. L. Collier and F. Singleton, *J. Appl. Chem.* **6**, 495 (1956).
4. G. L. Collier and A. C. M. Panting, *Spectrochim. Acta* **14**, 104 (1959).
5. E. C. Olson and C. D. Alway, *Anal. Chem.* **32**, 370 (1960).
6. A. Savitzky and M. J. E. Golay, *Anal. Chem.* **36**, 1627 (1964).
7. J. Steiner, J. Termonia and J. Deltour, *J. Anal. Chem.* **44**, 1906 (1972).
8. A. E. Martin, *Spectrochim. Acta* **14**, 97 (1959).
9. I. G. McWilliam, *Anal. Chem.* **41**, 674 (1969).
10. T. C. O'Haver and G. L. Green, *Anal. Chem.* **48**, 312 (1976).
11. A. T. Giese and C. S. French, *Appl. Spectr.* **9**, 78 (1955).
12. E. J. Cahill, *Int. Lab.* Jan/Feb., 64 (1980).
13. M. J. Hammer, *Water and Waste-Water Technology*, John Wiley & Sons, Inc., New York (1975).
14. R. J. Henry, *Clinical Chemistry, Harper & Row Pub. Inc.* New York (1964).
15. W. Maurer and J. Storp, *GIT Fachz. Lab.* **24**, 124 (1980).
16. M. Kortum and O. Kling, *Ärztl. Lab.* **18**, 33 (1972).
17. S. I. Walter, MTA—Journal **1**, 176, (1979).
18. Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Verlag Chemie, Weinheim (1979).
19. B. John, *Statistische Verfahren für technische Meßreihen*, Carl Hauser Verlag, München (1979).
20. J. Knoch, *Wasser und Boden*, **29**, 315 (1977).
21. J. Slanina, W. A. Lingerak, L. Bergman, *Z. Anal. Chem.* **280**, 365 (1976).