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Higher-Order Derivative Spectrophotometry in Environmental Analytical Chemistry†

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Higher-order derivative spectrophotometry (HODS) is a very good tool for the fine-resolution of spectra and other electric signals. This method allows one to separate superimposed curves for quantitative measuring. In the following, examples are given for the estimation of pollutants in water, air and soils which demonstrate the advantages of the HODS. This also applies to difficult problems in environmental analytical chemistry. In detail, we discuss the simultaneous estimation of aniline and phenol in waste water, the quantitative determination of PCP in polluted drinking water, phenol in turbid samples, the identification of aromatic amides and phenols in air after absorption in solvents and, last but not least, the study of Ni^{2+} adsorbed on bentonite powder.

KEY WORDS: Derivative spectrophotometry, environmental analysis, PCP, waste water, sheet silicates.

INTRODUCTION

Studies of the pollution of the environment and the influence and propagation of chemical substances in air, water and soil are based on many qualitative and quantitative analyses. Although the UV-VIS-Spectrophotometry is well suited for quantitative measurements at a constant wavelength, it is seldom applied to the characterization of different substances. That is due to the fact that dissolved substances or

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liquids and powders usually give less characteristic spectra with more or less developed maxima and shoulders.

Some years ago we showed that the higher-order derivative spectrophotometry (HODS) is a very powerful help for the fine-resolution and better interpretation of such electric signals.^{1,2} The various mechanical, optical and electrical methods employed in the last 30 years for the recording of derivative spectra (differentiation of signals) practically exploited first- and second-derivatives only. Occasionally, you find fourth-derivatives computed with digital methods. In our studies of the HODS we have now developed an analogue computer unit, with operational amplifiers, differentiators, separating modules and attenuators as well as active and passive filters which permit the first analogue on-line recording of low-noise, readily reproducible ninth-order derivative spectra. In practice, it is sufficient to record the 3rd to 5th derivative and, in some special cases, the 6th order.²⁻⁴

Sometimes low-order derivative spectrophotometry ($n \leq 2$) was applied to environmental analytical problems, e.g. to estimate the content of uric acid in waste water.⁵

This paper deals with the advantages of the application of higher-order derivatives to environmental analytical chemistry.

EXPERIMENTAL APPARATUS

All spectra were taken by a spectrophotometer SP8-100 (Philips Pye-Unicam, Cambridge). Solid substances were mixed in a micro vibration mill (Vibromill Beckman Instruments) with 1 up to ten parts of teflon (polytetrafluorethylen) or were directly pressed with a high pressure press (Beckman Instruments) to disks of 5 mm diameter and 0.2 mm thickness. They were positioned in a second cell holder directly at the multiplier to catch all stray light.

The derivatives were computed with an analogue differentiator TLB 6000^{2,3} (Lucius & Baer, Geretsried, F.R.G.; distribution: Pabisch, Munich). This apparatus is equipped with 3 operational amplifiers, 6 differentiators, 7 low-pass filters, separating modules and attenuators.

Mathematical operations were supplied by an "intelligent plotter" BS 8100 (Bascom-Turner Instr., Newton, Mass.). This apparatus is very well adapted to the manipulation of spectra and their derivatives, e.g. the superposition of signals, the standardization of spectra, the least square computation and smoothing functions, the logarithmic and derivative computation and also the storage of electric signals on floppies to organize a data bank.

For the simulation of standard turbidity the silica was dispersed in the samples by help of supersonics (Sonorex RK 102, Bandolin Electronic KG, Berlin; 35 KHz, 3 min).

RESULTS AND DISCUSSION

1. Water pollutants

Aniline and phenol are substances frequently found in industrial waste water. They are very toxic and therefore have to be kept under strict control. As the UV-spectra overlap in a bright region (Fig. 1), the superimposed curves (Fig. 2) are not suited for quantitative evaluation. On the contrary it is possible to estimate the amount of aniline and phenol by fourth- or fifth-order differentiation of the fundamental signal (Fig. 2). The distances \overline{AB} and \overline{EF} are proportional to the concentration of phenol, the distances \overline{CD} and \overline{GH} to those of aniline (Fig. 2). Linearity of concentrations to the peak height is shown in Figs. 3 and 4. In this case the highest deviations run to $\pm 3\%$ (phenol) and $\pm 5\%$ (aniline) respectively.

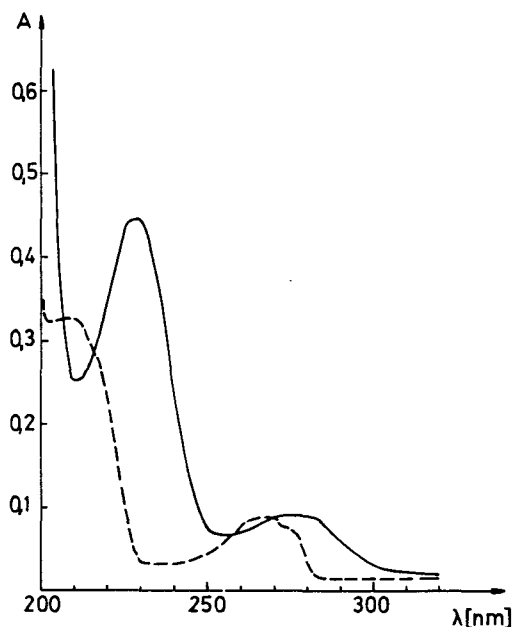


FIGURE 1 Spectra of 5 ppm aniline (—) and 5 ppm phenol (----) in water; LTH 1 cm, slit 1 nm, scan rate 2 nm/s.

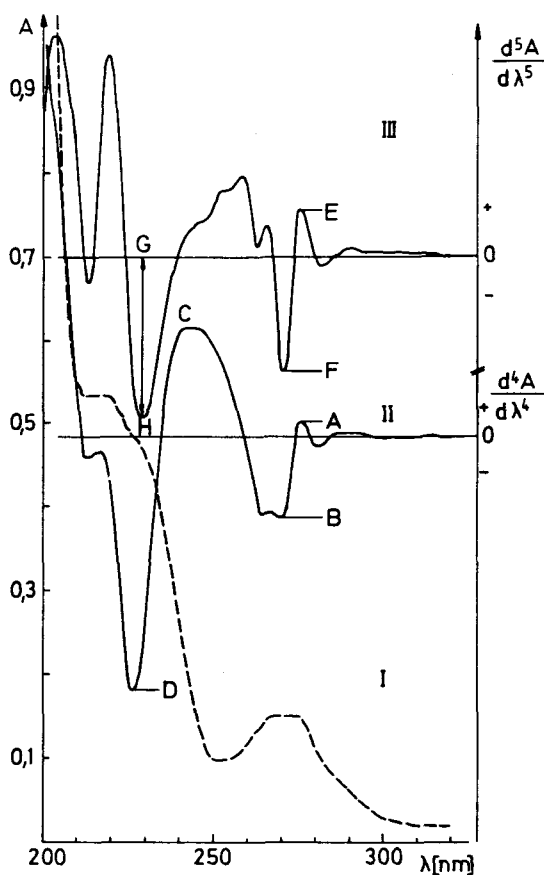


FIGURE 2 Fundamental spectrum (I, ----), fourth derivative (II) and fifth derivative (III) of a mixture of 5 ppm aniline and 5 ppm phenol in water. \overline{AB} and \overline{EF} is proportional to the concentration of phenol, \overline{CD} and \overline{GH} to the concentration of aniline; LTH 1 cm, slit 2 nm, scan rate 2 nm/s.

The simultaneous separation of the two superimposed spectra is a very good example and shows clearly which derivative order brings the better results. In the case of phenol the odd fifth derivative peak \overline{EF} is practically undisturbed (runs through zero) and optimal (Fig. 4). On the other hand, the even fourth derivative peak \overline{CD} of the aniline spectrum is indeed somewhat disturbed but more sensitive than the fifth one.

The estimation of the two compounds can easily be controlled automatically. In a bypass of a pipe-line a spectrophotometer, equipped with a tube pump and a continuous-flow-cell, takes spectra in definite

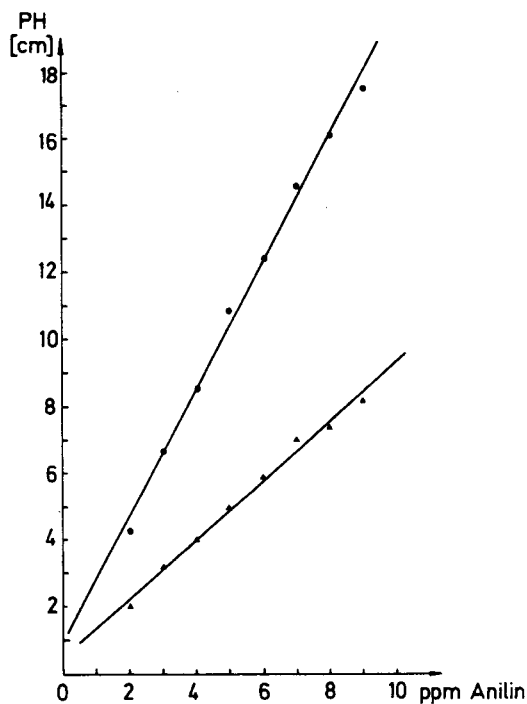


FIGURE 3 Standard curves for aniline in water with 5 ppm phenol; peak height (P.H.) w/v ppm aniline: $\circ-\circ-\circ$ fourth derivative (\overline{CD} in Fig. 2) and $\triangle-\triangle-\triangle$ fifth derivative (\overline{GH} in Fig. 2); same conditions as in Fig. 2 described.

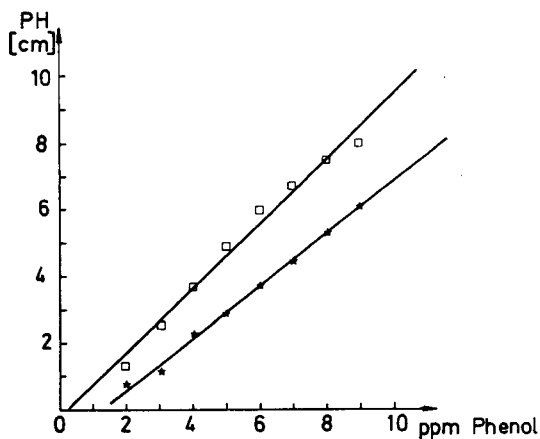


FIGURE 4 Standard curves for phenol in water with 5 ppm aniline; peak height (P.H.) w/v ppm phenol: $*-*-*$ fourth derivative (\overline{AB} in Fig. 2) and $\square-\square-\square$ fifth derivative (\overline{EF} in Fig. 2).

time interval (e.g. all 5 or 10 minutes). The concentrations of the hazardous substances are given by measuring the peak heights \overline{AB} (aniline) and \overline{CD} (phenol) in the control sheet (Fig. 5).

We succeeded also in the determination of micro amounts of pentachloro phenol (PCP) in water by a very simple but sensitive method. Up to 500 ppb PCP could be estimated by the help of HODS with a mean deviation of $\pm 4.2\%$, up to 50 ppb with $\pm 6.5\%$ respectively (Figs. 6a and 6b). Linearity of the function is strictly given (Fig. 6b).

2. Turbid samples

Waste water often contains more or less suspended solids or emulsified pollutants which disturb photometric analysis. In Fig. 7 the spectrum of 1 ppm phenol (I, ----) in clear water is disturbed when 1 mg/ml (II, ----) or 2.5 mg/ml (III, ----) aerosil (silica) is added and suspended. These superimposed spectra of the turbid samples are not qualified for quantitative estimations. But it is possible to eliminate the underground by higher order derivatives. Then the peak \overline{AB} is directly proportional to the concentration of the phenol and within $\pm 3\%$ constant.

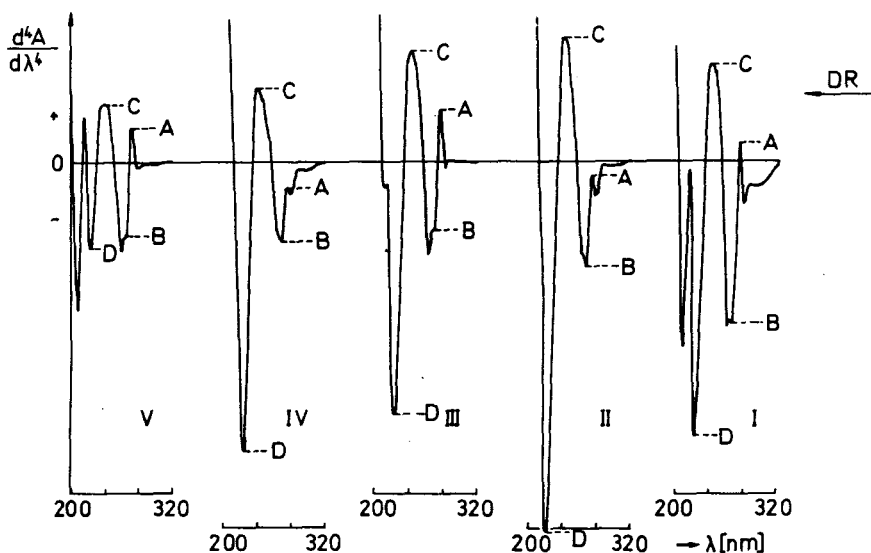


FIGURE 5 Control sheet of continuous simultaneous determination of aniline and phenol (fourth derivative); DR direction of registration. I: 5 ppm aniline, 8 ppm phenol; II: 7 ppm aniline, 5 ppm phenol; III: 5 ppm aniline and phenol; IV: 5 ppm aniline, 3 ppm phenol; V: 2 ppm aniline, 5 ppm phenol. LTH 1 cm, micro cell (10 μ l), slit 1 nm, scan rate 1 nm/s, registration cycle 5 min.

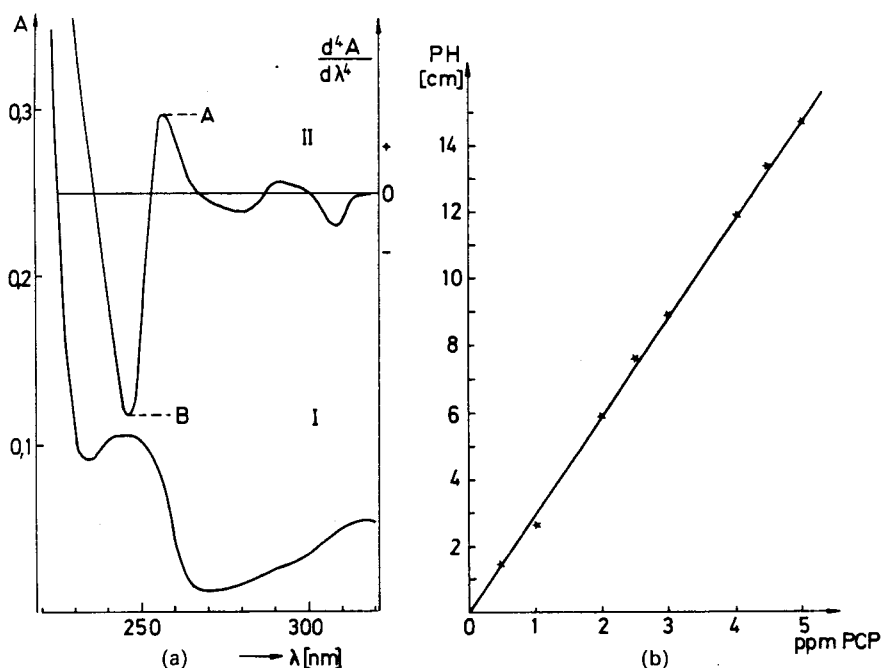


FIGURE 6 3 ppm pentachloro phenol (PCP) in 0.1 n NaOH. I: fundamental spectrum; II: fourth derivative of I; \overline{AB} is strictly linear proportional to the amount of PCP. LTH 1 cm, slit 1 nm, scan rate 2 nm/s.

3. Pollutants in air

Gases or vapours were first absorbed in a suited solvent and then analysed. We absorbed e.g. air-emitted benzene by conducting a definite volume of air through ethanol. In this way 1 ppm of the arene could be estimated in the 4th derivate with $\pm 5\%$ accuracy.²

With the help of UV/VIS HODS we were also able to identify fractions of various separation methods used for environmental analysis, e.g. chromatography, TLC, HPLC and others.^{2,3} "Fingerprints" of the substances were collected in a file. Some examples of higher-order fingerprints of aromatic amines and phenols are presented in Fig. 8. The pairs hydroquinone/naphthol-2 give similar, aniline/anisidine almost identical UV spectra which are hardly fit for identification. On the contrary higher-order derivatives show characteristic peaks in the fine resolved signals.

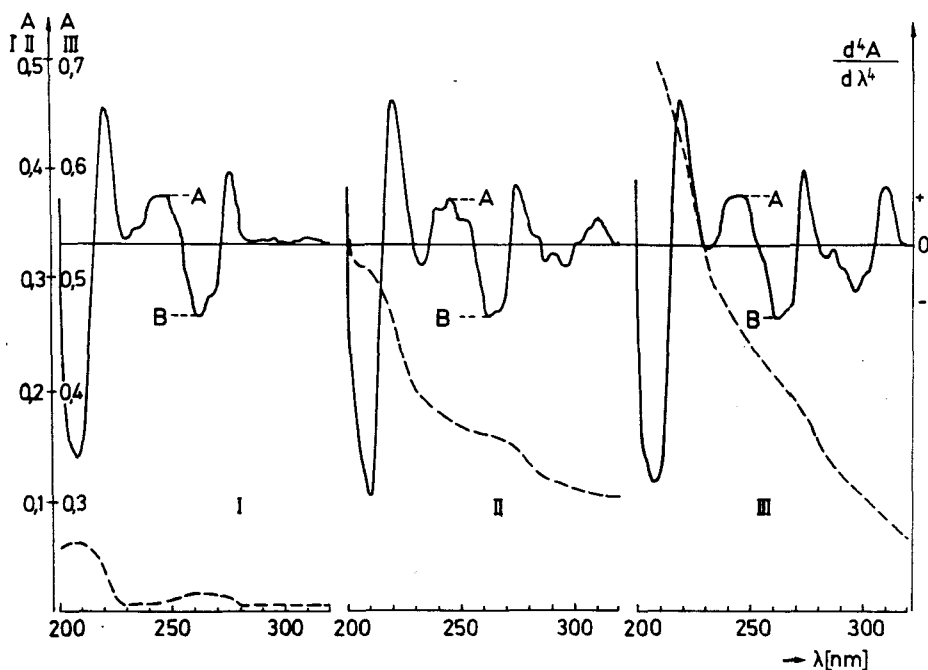


FIGURE 7 Spectra of phenol without and in the presence of silica (Aerosil®). I: 1 ppm phenol; fundamental spectrum (----) and fourth derivative (—); II: 1 ppm phenol and 1 mg/ml suspended silica. III: 1 ppm phenol and 2.5 mg/ml suspended silica. \overline{AB} is proportional to the concentration of phenol. LTH 1 cm, slit 1 nm, scan rate 2 nm/s.

4. Pollutants in soil

UV/VIS spectra of solids usually are of very little evidential value, whereas their HOD are much better to interpret. We made use of this effective method to study the adsorption of Cu^{2+} , Co^{2+} and Ni^{2+} on sheet silicates. These minerals together with humic acids, are very interesting and important for the adsorption and desorption mechanism of potassium, ammonium or heavy metals in soils and deposits.

To demonstrate the advantage of higher-order derivatives for the fine-resolution of electric signals, the fundamental spectra and their 6th derivatives of pure bentonite and bentonite treated with Ni^{2+} were taken (Fig. 9). The peak \overline{AB} is proportional to the concentration of the transition metal. Bentonite treated with Co^{2+} or Cu^{2+} leads to similar results.

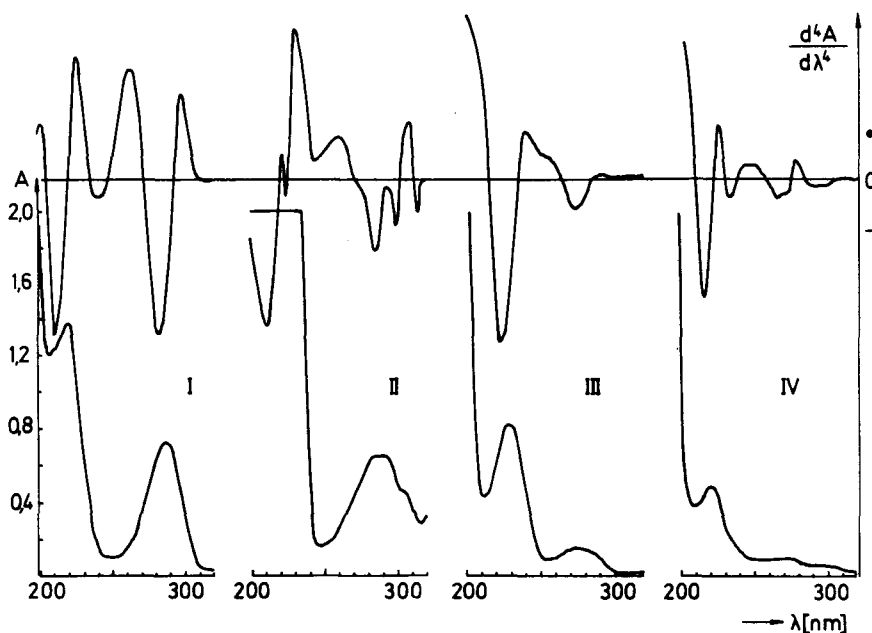


FIGURE 8 Fundamental spectrum and fourth derivatives of some organic compounds in water. I: 30 ppm hydroquinone; II: 20 ppm naphthol-2; III: 10 ppm aniline; IV: 10 ppm anisidine. LTH 1 cm, slit 1 nm, scan rate 2 nm/s.

CONCLUSIONS

The cited studies demonstrate that the use of higher-order derivatives is very effective in the environmental analysis. This applies especially to the determination of micro amounts of hazardous chemicals and the investigation of suspensions and solids.

Among the preconditions for the obtaining of reproducible results are low-noise spectrophotometric signals and low-noise derivative modules. According to our experience we are of the opinion that low-pass filtering or signal averaging is the best method for the removing of noise. Smoothing functions indeed results in greater signal-to-noise ratios (SNR), but the curves are more or less pulled out of shape. This becomes evident when taking higher-order derivatives which differ from untreated signals in peak height and fine structure.

While in low-order derivatives one may neglect the shifts of the peaks, in higher-order differentiation the deviations are greater and must be

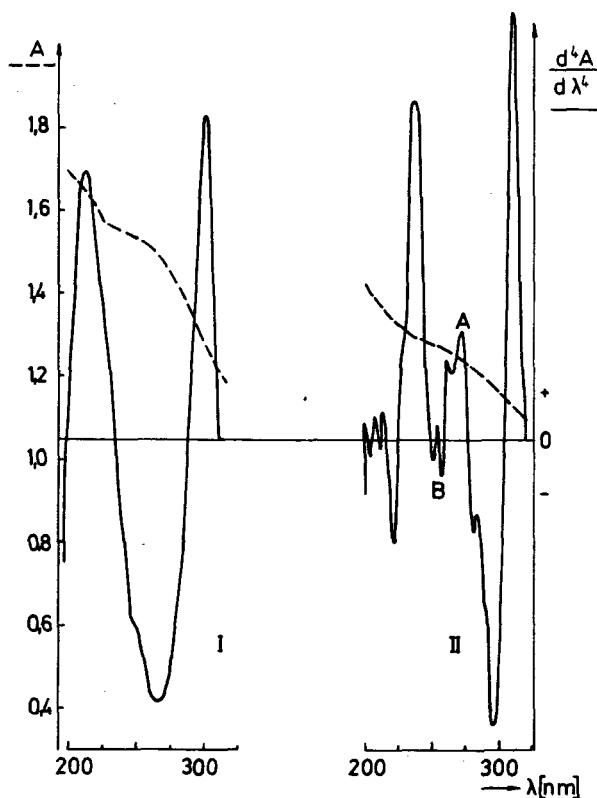


FIGURE 9 Untreated bentonite (I) and bentonite with adsorbed Ni^{2+} (II); \overline{AB} is proportional to 1.65 meq Ni^{2+} /g bentonite. Fundamental spectra (----) and fourth derivatives (——). Powders were placed between two silica plates (distance 0.2mm) and positioned in front of the multiplier.

corrected if the rear position of the signals is wanted. This is true for analogue as well as digital computations. In quantitative estimation corrections were not necessary because only the amplitudes of the peaks were evaluated.

When the appropriate low-pass-filters and low-noise differentiating modules are used, the higher-order derivative spectrophotometry is an excellent method to solve difficult problems in environmental analytical chemistry.

Acknowledgements

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