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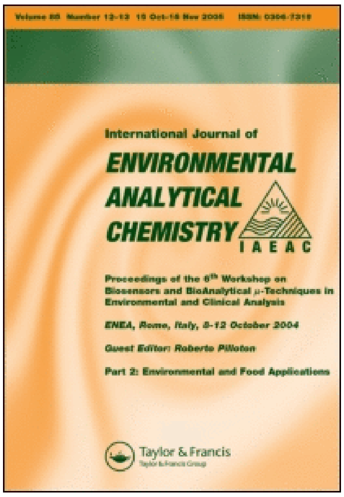

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State Of The Art For The Examination Of Uv Spectra Of Waters And Wastewaters

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STATE OF THE ART FOR THE EXAMINATION OF UV SPECTRA OF WATERS AND WASTEWATERS

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The paper reviews different mathematical methods for the exploitation of the UV spectrum of waters and wastewaters, including the interferences treatment. After the presentation of simple methods and their limits, several global approaches using a matricial presentation of the data are discussed. The usual methods, statistical multivariate or deterministical procedures are not relevant. Nevertheless, other methods based on the restitution of interferences effect as a combination of fixed basic signals, either mathematical or physical, are available. The first procedure is semi-deterministic without chemical knowledge of the interferences nature or effects—and only mathematical hypothesis on the spectrum shape—while the second is a more qualitative method based on the fact that most of interferences can be resumed as a linear combination of few independent spectra with chemical signification. These considerations underline the importance of direct examination of UV spectra of waters and wastewaters.

KEY WORDS: UV absorptiometry, water analysis, chemometrics.

INTRODUCTION

The use of UV absorptiometry for the assessment of waters and wastewaters quality is increasing with the need for specific compounds measurement and for the estimation of organic pollution. The first and simplest method[1] uses a relation between the absorbance at one wavelength (usually 254 nm) and the global determination of organic matter (BOD, COD, ...). Few derivative methods are used for nitrate and phenolics determination[2], and multiwavelength absorptiometry[3] for nitrate[4] and chromium VI[5]. However, no classical

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statistical methods have been proposed, like for example multivariate or partial least squares methods[6]. Finally, some recent developments, derived from the use of Fourier transformed functions[7,8] or from a semi-deterministic macroscopic method[9], have been proposed. The aim of this paper is to compare different mathematical methods, especially those including interference treatment of the UV signal.

GENERAL PRINCIPLES

The basic problem to be addressed is the determination of the concentrations (C_1, C_2, ..., C_p) of p absorbent specific components of a water or a wastewater sample. The analytical procedure is complex because of the presence of interferences: suspended solids—for raw samples—colloidal materials and other dissolved components. The data are the absorbances $A(\lambda_i)$ of the sample, measured for all the wavelengths $\lambda_1, \lambda_2, \ldots, \lambda_n$ (with n>>p). In a first step, we assume that the nature of the components is known, and also their absorptivities $e_1(\lambda), e_2(\lambda), \ldots, e_p(\lambda)$ for all the wavelengths. For a diluted solution the Beer-Lambert relation can be applied:

$$A(\lambda) = \sum_{k=1}^{p} C_k.e_k(\lambda) + I(\lambda) \tag{1}$$

where C_k is the concentration of the component k, and $I(\lambda)$ the interference value, or the value of the absorbance resulting of the effect of all the components existing in the solution except the p components to be measured.

The sum of the absorbances of the specific components will be called the signal value. In fact, the absorbance is known with an error, bound to the spectrophotometer characteristics, but its value is supposed stochastical and moreover negligible.

Least squares methods

The first method for the determination of concentrations is the multicomponents method which is used in almost all spectrophotometers. It computes an approximation of the concentrations as a least-squares solution of the matrix resolution:

$$\begin{pmatrix} e_1(\lambda_1) & \ldots & e_p(\lambda_1) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ e_1(\lambda_n) & \ldots & e_p(\lambda_n) \end{pmatrix} . \begin{pmatrix} C_1 \\ \cdot \\ \cdot \\ \cdot \\ C_p \end{pmatrix} = \begin{pmatrix} A(\lambda_1) \\ \cdot \\ \cdot \\ \cdot \\ A(\lambda_n) \end{pmatrix} \tag{2}$$

This method gives very poor results because it considers the interference $I(\lambda)$ as negligible or stochastical, which is never the case. A study of several types of interferences (without specific components) shows that the shapes are often similar (Figure 1) and this phenomenon will be studied later. This consideration is valuable for other methods, also based on the least squares computation, which do not consider the effect of the interference[6]. Sometimes, the interference $I(\lambda)$ can even be more important than the signal.

Because of those reasons, we must use another method based on the reconstitution of the interferences, simulated as a linear combination of reference spectra $S_1, S_2, \ldots, S_q$ (notice that q+p, number of components to be computed must be much lower than n, number of measured absorbance values):

$$I(\lambda) = \sum_{j=1}^{q} a_j.S_j(\lambda) + I_{res}(\lambda) \tag{3}$$

where i_{res} is called residual interference.

The adjustment of the a_j coefficients is performed at the same time as the computation of the p concentrations Ck of the specific components, in order to minimise the residual absorbance and to make their variations as stochastical as possible. A first approximation is obtained by the basic least-squares resolution of the relation:

$$M \;.\; \begin{pmatrix} a_1 \\ \vdots \\ a_q \\ C_1 \\ \vdots \\ C_p \end{pmatrix} = \begin{pmatrix} A(\lambda_1) \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ A(\lambda_n) \end{pmatrix} \tag{4}$$

where

$$M = \begin{pmatrix} S_1(\lambda_1) & \ldots & S_q(\lambda_1), e_1(\lambda_1) & \ldots & e_p(\lambda_1) \\ \cdot & & \cdot \quad \cdot & & \cdot \\ \cdot & & \cdot \quad \cdot & & \cdot \\ \cdot & & \cdot \quad \cdot & & \cdot \\ S_1(\lambda_n) & \ldots & S_q(\lambda_n), e_1(\lambda_n) & \ldots & e_p(\lambda_n) \end{pmatrix}$$

Some improvements of the performances have been tested using other optimisation criteria, such as weighting methods from qualitative properties of interferences. But the detection limit and the precision of the calculation of concentrations mainly depend on the choice of the reference spectra and of the wavelength interval.

Transformed methods with scalar products

The definition of the scalar product between the spectra S and S′ can be:

$$<S, S'> = \sum_{i=1}^{n} S(\lambda_i).S'(\lambda_i) \tag{5}$$

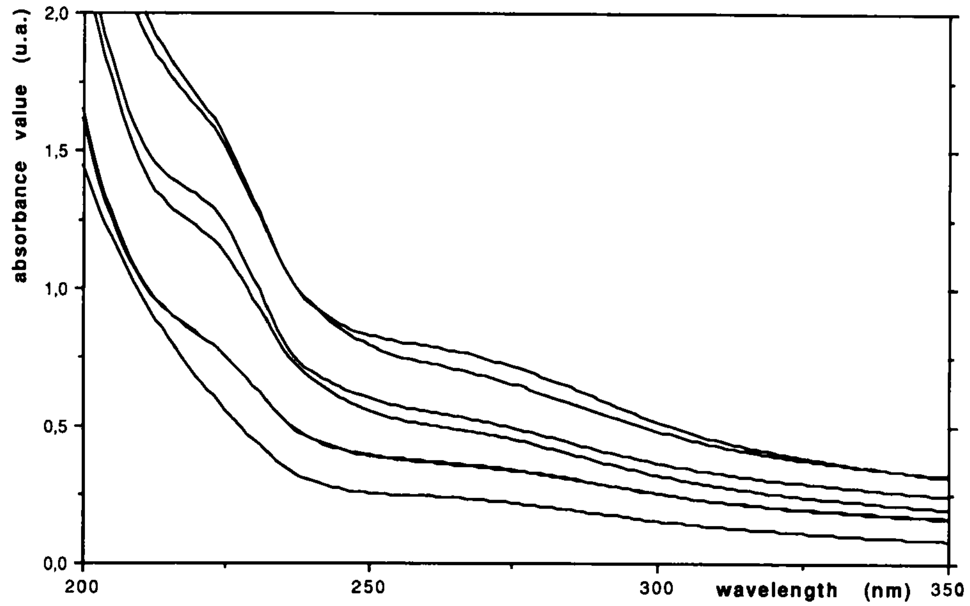

Figure 1 UV spectra of different urban wastewaters.

or

$$<S,S'> = \int_{-\infty}^{+\infty} S(\lambda).S'(\lambda).d\lambda$$

Classical mathematical methods allow to build a basis of algebraic analytic functions F_1, …, F_q, … which are orthonormal with respect to this scalar product (i.e. $<F_i, F_j> = 0$ if $i \neq j$ and $= 1$ if $i = j$). From a spectrum U(1), its transformed function can be built as the file ($\hat{U}(1)$, …, $\hat{U}(q)$, …) given by $\hat{U}(j) = <U,F_j>$.

So, we have by transforming the relation (1):

$$\hat{A}(j) = \sum_{k=1}^{p} C_k.\hat{e}_k(j) + \hat{I}(j)$$

The principle is choosing the Fj basis, in order that $\hat{I}(j)$ vanishes for $j = j_1, \ldots, j_p$ and the transformed signal values $\hat{e}_k(j)$ are significant for the same values: so we get a physical separation of the spectra with a mathematical method. The concentration approximation is then computed by solving the following system:

$$\begin{pmatrix} \hat{e}_1(j_1) & \ldots & \hat{e}_p(j_1) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \hat{e}_1(j_p) & \ldots & \hat{e}_p(j_n) \end{pmatrix} . \begin{pmatrix} C_1 \\ \cdot \\ \cdot \\ \cdot \\ C_p \end{pmatrix} = \begin{pmatrix} \hat{A}(j_1) \\ \cdot \\ \cdot \\ \cdot \\ \hat{A}(j_p) \end{pmatrix} \qquad (6)$$

A classical example of the use of this method is the Fourier transform, where the F_j's are chosen as trigonometric functions. Another method[10] uses the F_j's as orthogonal polynomials.

The performances of this method also depend on the choice of the basis of functions F_j which has to be adapted to the mathematical properties of the interference spectra to be cancelled.

Mixed method

In this method we also use an orthonormal basis of spectra F_j but it is extracted by linear combinations from the reference spectra S_j. As previously the transformed function $\hat{U}(j)$ of the spectrum $U(\lambda)$ is defined:

$$U(\lambda) = \sum_{j=1}^{q} \hat{U}(j).F_j(\lambda) + U_{res}(\lambda)$$

and

$$A_{res}(\lambda) = I_{res}(\lambda) + \sum_{k=1}^{p} C_k.e_{kres}(\lambda) \qquad (7)$$

If the choice of the reference spectra is appropriate, $I_{res}(\lambda)$ is small and the residual signals $e_{kres}(\lambda)$ are significant. The approximations of concentrations are computed from the following system deduced from (7):

$$M' . \begin{pmatrix} C_1 \\ \cdot \\ \cdot \\ \cdot \\ C_p \end{pmatrix} = \begin{pmatrix} <A,e_{1res}> \\ \cdot \\ \cdot \\ \cdot \\ <A,e_{pres}> \end{pmatrix} \qquad (8)$$

where M' is the matrix of p lines and p rows with general term: $m'(i,j) = <e_{ires},e_{jres}>$, and $<A,e_{ires}>$ is the scalar product of the measured absorbance and the residual absorptivity e_{ires}.

From a theoretical point of view, the approximation obtained with this method is similar to that given by the least squares method with interference restitution. However the computation time is reduced and the truncature errors are limited. This last point is very important when the ratio between the highest and the lowest eigenvalues of the matrix ${}^tM.M$ (which occurs in the resolution of (4)) increases.

Other improvements of the numerical aspects are possible: for example, the Q-matrix approach[11] provides the possibility of using different reference spectra and gives more robust results than the basic least-squares method. However, the main limitation is that they are more qualitative than numerical.

As we have to assume that the possible interferences are spanned by an infinite number of spectra, most of the possible choices of the reference spectra give a great bias in the reconstitution of the interferences[12]. Therefore the main problem is knowing if this reconstitution is possible when the number of reference spectra is limited (for example at most 5 or 6). In that case we have to identify these spectra among all the others.

"ALL MATHEMATICAL" CHOICE

The criteria for the choice of the reference spectra $S_1, \ldots, S_q$ or the orthonormal spectra $F_1, \ldots, F_q, \ldots$ will be given below. These spectra are mathematical functions whose chemical significance is non existent. They will include the permanent qualitative properties of the interferences. These properties are mathematical but their validity is based on chemical considerations.

Generalities

The mathematical theory shows that there is a basis of functions $u_1, \ldots, u_j, \ldots$, so that any function $S(\lambda)$ can be approached (in the inside of a given interval) by the function:

$$SN(\lambda) = \sum_{j=1}^{N} a_j . u_j(\lambda)$$

called approximation of N order.

For example, the approximation by Fourier series uses the choice of:

$$u_j(\lambda) = \exp(\sqrt{-1}.(j-1).\lambda)$$

and the polynomial approximation uses the basis:

$$u_j(\lambda) = \lambda^{j-1}$$

Other approximations are possible by using a basis of linear functions or of spline functions. In fact this mathematical consideration is crude and therefore unusable for the separation of the signal from the interference. The most important property is not that the approximation error $|S(\lambda)-SN(\lambda)|$ becomes small when N increases, but that its convergence is faster when the function S is more regular (the successive derivatives are very small). The separation of the signal from the interference proves that the interference is more regular than the signal. We consider the interference is constituted by a very great number of components, each of them having a very low concentration. The theoretical spectrum of the interference (at zero Kelvin and without solvent contribution) can be composed of many little peaks. However, the signal can be constituted by few important peaks. Actually the temperature and the solvent effect cause the resulting shape to be very smooth and this regularisation is faster when the initial distribution of the peaks is denser. The experimentation indicates that this assumption is true for natural waters or urban wastewaters, and the proof is given in a previous paper[3]. For industrial wastewaters this model is less accurate and, as a result, the error is greater.

UV multiwavelength absorptiometry

This method[3] uses the least squares with the restitution of interference, or the mixed method, and the interference spectra are chosen as polynomial functions: $S_j(\lambda) = \lambda^{j-1}$. Actually, the results are quite good when the number of components to be determined is small (1 or 2), and when their absorptivity spectrum is perturbed. Within a given interval (for example if there is a peak) when the interference spectrum is regular, we get the area of the determination of nitrate[4] or chromium VI[5] in natural waters or urban treated wastewaters (Figure 2). In fact, the convergence of the polynomial approximation requires very drastic conditions of regularity for the interference, so the wavelength interval chosen for the computation has to be as small as possible and well selected. The replacement of the polynomial basis S_j by other basis as linear functions or spline functions allows us to work on greater intervals, especially with a penalization procedure. It is important to note that the problem can be more complex if the shape of specific absorptivity spectra varies with pH for example. In this case, we have to consider the different forms of the component spectra for the extreme conditions[5].

It is important to evaluate the approximation error in order to optimise the method. The approach is simplified by considering only one component; its concentration C* is computed from the relation (8):

$$C^* = \langle A, e_{1res} \rangle \ / \ \langle e_{1res}, e_{1res} \rangle \qquad (9)$$

If we take into account relation (1), we obtain by considering the orthogonality of the spectra $F_1, \ldots, F_q$ and e_{1res}:

$$\Delta C = C^* - C = \langle I_{res}, e_{1res} \rangle \ / \ \langle e_{1res}, e_{1res} \rangle$$

and so,

$$\Delta C \leq (\langle I_{res}, I_{res} \rangle \ / \ \langle e_{1res}, e_{1res} \rangle)\ \tfrac{1}{2} \qquad (10)$$

This relation confirms that the error ΔC depends on the ratio between the residual interference and the residual signal, which is small when I is more regular than the signal. Moreover, the optimisation of the method (choice of the q reference spectra and of the wavelength interval) leads to minimising the error, or to maximising the residual signal and keeping the residual interference small. The best result is given when the interference is well approximated and the signal badly computed by linear combinations of $S_1, \ldots, S_q$. Therefore, the increase of the number q of reference spectra is not the best choice.

But the usual estimations of the error given by the statistical literature cannot be used here, as they assume that the residual interference is drastically stochastical. For each wavelength the error follows a Gaussian distribution whose standard value is independent

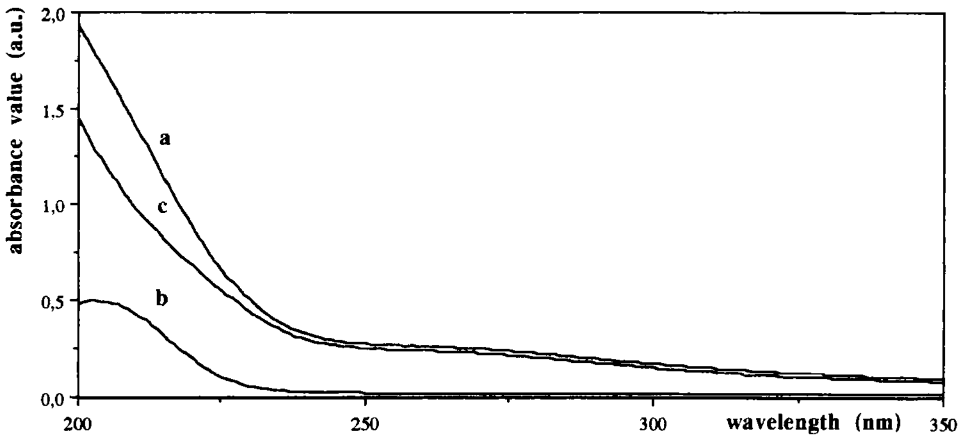

Figure 2 UV spectrum of a treated wastewater with 3.8 mg/l nitrate (a) and resulting spectra after multiwavelength absorptiometry computation: nitrate (b) and interference (c).

of the wavelength. This condition is rarely found and it is shown by the study of the residual values. Further analysis shows that these biases are still present in our method for the model we use (approximation of the interference by polynomials of small degrees). On the other hand, the last relation (10) provides a deterministic upper bound of the error, which is not a statistical estimation: so it is not subject to bias. Although this bound cannot be precisely computed, it gives a criterion for keeping the error small, and this error assumes coarse qualitative properties of the interferences. However, a more refined reconstitution of the interference is possible as it will be shown in the last part.

Transformed methods

Theoretically the Fourier transform is able to increase the signal to interference ratio for some frequency values, and also simulate by deconvolution the inverse process earlier described of peak diffusion. This means to show the initial theoretical absorption peaks. This method is useful for the interpretation of the IR spectra but not for the UV ones[7], because the Fourier transform works with a signal entirely defined (with zero values outside the interesting interval) as in the case of IR bands. An UV spectrum is not entirely known because the spectrophotometers limit their scanning to 200 nm in order to prevent oxygen absorption. Moreover, the shape of any UV spectrum of waters always decreases from 200 to 350 nm and never vanishes around 200 nm except for water of ultra high quality. The truncature of a function strongly disturbs the Fourier transform on the whole interval where the transformed function is computed. This is because any local singularity disturbs the whole transformation.

A modification of the Fourier transform called wavelets transform[8] is able to reduce this truncature effect. The principle is based on the construction of daughter wavelets from a mother one f(λ), oscillating and exponentially decreasing:

$$f_{a,b}(\lambda) = \sqrt{a}.f(a.(\lambda - b))$$

The wavelets transformed spectrum of S is defined by:

$$S(a,b) = <S,f_{a,b,}> = \int_{-\infty}^{+\infty} S(\lambda).f_{a,b}(\lambda).d\lambda$$

The choice of the mother wavelet is very important for the elimination of the interference. As an example, a test was conducted by adding a synthetic interference signal of Gaussian form including (in the middle of the slope) another Gaussian signal, in order to have a maximal signal to noise ratio of 1/50. After the determination of the wavelets transform the ratio is inversed and becomes close to 100.

SEMI DETERMINISTIC MACROSCOPIC METHOD

The starting point is the comparison of spectra of different samples of a wastewater network[13] and this experimentation shows isosbestic points for some set of spectra, namely in relation to the mixing of waters. A theory for the interpretation of a set of spectra has recently been proposed[9].

Starting from a great number of spectra $SM_1, ..., SM_n$ which are supposed to represent different states of a mixture varying with time, with space or with the characteristics of interferences, it can be supposed that there are particular spectra $SR_1, ..., SR_q$, called reference spectra. These spectra constitute a basis of independent spectra for the restitution of the n-q others (q<<n). The linear combination of the reference spectra is expressed as follows:

$$SM(\lambda) = \sum_{j=1}^{q} a_j.SR_j(\lambda) \pm r \qquad (11)$$

where, aj is the coefficient of the j[th] reference spectra and r is the admitted error.

The number q of independent spectra is the rank of the system $\{SM_1, ..., SM_n\}$ whose knowledge is very useful for:

-the study of the composition of mixtures (as for the interpretation of a chromatogram[10]),

-the detection of the occurrence of another specific component into the water if the rank varies with a new sample. The eventual identification and concentration measurement is possible if the corresponding spectrum (S_a) exists as a file of the procedure. In that case, the concentration measurement is performed by using one of the numerical methods described in the first section, where $SR_1, ..., SR_q$ provide the reference spectra for the reconstitution of the interferences.

Mainly, the result of the semi deterministic macroscopic method is finding reference spectra (for different samples) which are almost identical from one type of water to another. Therefore, an underground determinism, which has a chemical explanation, could exist. This assumption will be studied in another paper, but the coherence of this "mathematically detected" determinism with chromatographic verifications has already justified this research[14].

CONCLUSION

From this work we may conclude the limitation of the very simple methods for the examination of the UV spectrum of the waters. Second, the more complex methods and particularly of all statistics with no treatment of the interferences, are inappropriate. On the contrary, the methods based on the restitution or the elimination of the interferences are well suited to the purpose. Moreover, the semi deterministic method is very useful for the comparison of the shape of the spectra and the qualitative knowledge of the absorbent material of waters and wastewaters.

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