

# Issues concerning spectral analysis of water samples for monitoring and treatment of public water resources

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## ABSTRACT

Experimental measurements conducted in the laboratory, involving hyperspectral analysis of water samples taken from public water resources, have motivated a re-evaluation of issues concerning the potential application of this type of analysis for water monitoring, treatment and evaluation prior to filtration. One issue concerns hyperspectral monitoring of contaminants with respect to types and relative concentrations. This implies a need to better understand the statistical profiles of water contaminants in terms of spatial-temporal distributions of electromagnetic absorption spectra ranging from the ultraviolet to infrared, which are associated with specific water resources. This issue also implies the need to establish correlations between hyperspectral signatures and types of contaminants to be found within specific water resources. Another issue concerns the use of absorption spectra to determine changes in chemical and physical characteristics of contaminants after application of water treatments, in order to determine levels of toxicity with respect to the environment. This paper presents a prototype spectral analysis showing various aspects relevant to water monitoring and discusses the use of basic theory for the interpretation of spectral features associated with water contaminants, as well as discussing inverse analysis of hyperspectral measurements.

**Key words** | absorption spectra, contaminants, spectral analysis, water monitoring

## INTRODUCTION

Experimental measurements conducted in the laboratory, involving hyperspectral analysis of water samples taken from public water resources, have motivated a re-evaluation of issues concerning the potential application of this type of analysis for water monitoring, treatment and evaluation prior to filtration (Bryant & Yapijakis 1977; Yapijakis 1983; Beemster & Schlager 1991; Crittenden *et al.* 2012). One issue concerns spectral monitoring of contaminants with respect to types and relative concentrations. This implies a need to better understand the statistical profiles of water contaminants in terms of spatial-temporal distributions of electromagnetic absorption spectra ranging from the ultraviolet to infrared, which are associated with specific water resources. This issue also implies the need to establish correlations between spectra and types of contaminants to be found within specific water resources. Another issue concerns the use of absorption spectra to determine changes in chemical and physical characteristics of contaminants

after application of water treatments, in order to determine levels of toxicity with respect to the environment.

In what follows, results of experimental measurements and theory based calculations are presented. A discussion of these results examines their relevance for monitoring water contaminants using hyperspectral measurements and possible pathways for achieving this goal. It is significant to note that this discussion does not consider any specific procedure for the 'solution' of the problem, but rather a general 'posing' of the problem, which is in light of the experimental measurements and theoretical calculations described here. In particular, the problem to be posed is as follows: to what extent can hyperspectral measurements and post analysis of these measurements be used for quantitative water monitoring?

With respect to this problem, our purpose is to describe conceptually a water monitoring methodology for potential application, as well as providing some proof of this concept.

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Accordingly, all analyses that follow are prototypical and only for proof-of-concept.

As routinely conducted, spectrophotometric or colorimetric analysis of water quality parameters in the visible spectrum rely on comparison of spectral readings at optimum (for each parameter) wavelengths for the actual water sample versus a stored calibration curve of solutions of the parameter in deionized water. This may require the addition of chemicals to the sample and deionized water solutions in order to generate a specific color related to the specific water quality parameter to be read. The interference of all other water sample quality parameters is negated by matching a blank to the zero of the calibration curve. Hyperspectral analysis considers the spectrum extending from ultraviolet to infrared. Our proposed hyperspectral analysis of water samples seeks to achieve a result similar to fingerprinting, where a number of points are matched resulting in statistical certainty. In our analysis, we expect to have a number of match points or readings from the ultraviolet through visible to the infrared spectrum that would allow us to achieve statistically accurate determination of particular water quality parameters, by comparing those readings to a database of similar hyperspectral measurements of samples, in terms of their parameterization, from a collection of water resources. The problem as posed implies consideration of not only issues related to feasibility but also sensitivity concerning correlation of spectral signatures with types and relative levels of water contaminants.

The theoretical foundation of our approach is similar to that of hyperspectral imaging using remote sensors. Accordingly, hyperspectral imaging represents the background of our approach in terms of its formal structure (Landgrebe 2002; Louchard *et al.* 2002; Govender *et al.* 2007; Bhatti *et al.* 2010; Friese *et al.* 2010; Pierna *et al.* 2012; Chang 2013). Govender *et al.* (2007) present a comprehensive review of hyperspectral remote sensing. Our spectral analysis approach is significantly different, however, both in terms of type of measurements and analysis procedure. In contrast to hyperspectral imaging, which uses remote sensor reflectivity measurements to construct a spatial distribution of intensities (i.e., an image), our approach uses transmission measurements for construction of a database of model parameters where issues of spatial resolution are not relevant. The spectral analysis procedure of our approach is that of inverse analysis, which entails parameter estimation for parametric model representations of transmission spectra (Brown 2006; Shubitidze & Osterberg 2007; Stancik & Brauns 2008). These model parameters, which provide an optimal encoding of spectral signatures,

can in principle comprise the contents of databases for characterization of water systems.

The organization of the subject areas presented here are as follows. First, a general discussion is presented concerning aspects of the spectral analysis of water samples and of its significance for enhancement of capabilities associated with water monitoring. Second, a prototype spectral analysis is presented showing various aspects relevant to water monitoring. Third, a general discussion is presented concerning the use of basic theory for interpretation of spectral features associated with water contaminants. Fourth, a discussion concerning inverse analysis of hyperspectral measurements is presented. Finally, a conclusion is given.

## SPECTRAL ANALYSIS OF WATER SAMPLES

There exist mature capabilities for water monitoring and decontamination, in particular, hyperspectral sensors and ozonation of water contaminants (Bryant & Yapijakis 1977; Yapijakis 1983; Beemster & Schlager 1991; Crittenden *et al.* 2012). These capabilities, however, can be enhanced for the purposes of water monitoring and decontamination using parametric model representations, in conjunction with their spectral signature interpretation, before and after water treatment processes that deactivate contaminant toxicity, such as ozonation. Being able to model the signatures of water and their contaminants will allow better interpretation of spectral features, which can optimize both water monitoring algorithms and treatment processes.

Water monitoring based on analysis of spectral signatures poses a significant problem owing to the wide variability of ambient environments associated with waterways, e.g., groundwater environments and reservoirs (Beemster & Schlager 1991). Quantitative monitoring of water and contaminants via spectra requires the construction of water-system-specific databases of spectra. These databases are constructed by sampling over time, for specified locations within specific water environments, e.g., rivers and various types of ground water environments, and hyperspectral measurements associated with this sampling, i.e., transmission. The utility of a given database will depend upon its adaptability for spectral signature isolation and correlation with various types of water contaminants. The correlation of spectral signatures with various types of water contaminants defines an inverse problem. This inverse problem must address two major aspects of water contamination: the statistical variability of spectra that are measured for sampling within specific water

environments, containing both contaminants and nontoxic materials, extending over long time periods; and the inherent complexity of the absorption spectra of chemicals and materials dissolved in water.

Inverse analysis of spectra having variability with time requires isolation of statistically significant features of the spectra that can be correlated with a specific water environment (Brown 2006; Stancik & Brauns 2008). This problem can be addressed by noting that, although the relative percentages and types of materials dissolved in a given water environment can vary nondeterministically, a given water environment can be associated with a well-defined statistical ensemble of spectral signatures. This follows from the fact that, although the relative percentages and types of materials will vary, this variation will occur within limits. In principle, for a given water environment, its associated ensemble of spectral signatures should be uniquely defined. Accordingly, databases for spectra must be structured to include not only spectral signatures and their correlation with various types of additives, but also ensembles of spectral signatures corresponding to specific water environments. Inverse analysis of spectra associated with water containing dissolved chemicals presents a particular problem in terms of correlation of spectral features with specific molecules given that the hyperspectral response of different types of molecules in solution is not in general known and thus not documented for potential inclusion into databases.

The absorption coefficient  $\alpha$  as a function of wavelength provides a method for understanding the relationship between spectral features and specific molecules in solution (see Bohren & Huffman 2004). To a first order approximation, measurement of  $\alpha$  is via the relationship

$$I = I_0 \exp(-\alpha d) \quad (1)$$

where  $I$  and  $I_0$  are the transmitted and incident intensity, respectively, and  $d$  is the thickness of the sample. In that all spectral analysis for water monitoring is with respect to an ambient water environment, a primary reference component of a database should be the absorption coefficient of chemically pure water. For any spectral analysis of water contaminants this quantity establishes the range of frequencies corresponding to windows of transmission, as well as windows associated with partial transmission, through an ambient water background. Another primary reference component of a database should be values of  $\alpha$  corresponding to solutions containing a single additive component, e.g., pure iron in water, or in general, relatively

simple solutions. Again, these quantities can be determined using inverse methods of spectra analysis. In addition, associated with these quantities can be values of  $\alpha$  obtained theoretically, using calculations based on density function theory (DFT) and time-dependent-DFT (Hohenberg & Kohn 1964; Runge & Gross 1984). These calculated spectra can provide physical interpretation of processes associated with the measured spectra.

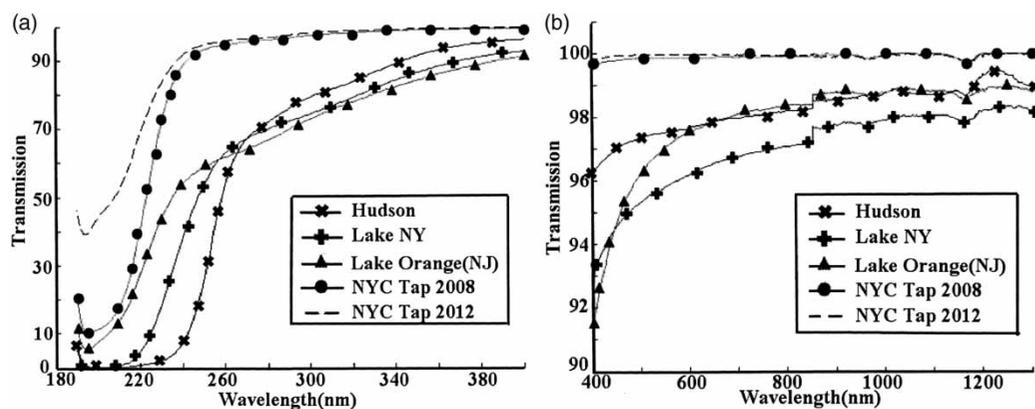
## PROTOTYPE SPECTRAL ANALYSIS

In this section, a prototype analysis is presented for the purpose of showing various aspects of spectral analysis of water samples associated with water monitoring in practice. The prototype analysis uses water samples obtained from various water resources in the New York City area. The water samples were measured using a Perkin-Elmer™ Lambda 900 UV/Vis/IR spectrometer (Shelton, CT) in transmission mode.

For this prototype study, the Cooper Union Environmental Research Laboratory (NYC) collected and supplied to the Naval Research Laboratory a series of water samples obtained from various water resources in the New York City metropolitan area, and a couple collected from the same sources at different times. The water sample sources varied from NYC's chemically treated tap water, to several lakes, to the East and Hudson Rivers and, therefore, they varied greatly in the level of concentration and the types of water quality parameters contained therein. This is represented by the type of spectral variations that are shown in Figure 1. For instance, NYC's tap water is comparative to the quality of the lake water, with primarily soluble compounds and colloids but with fewer pollutants and bacteria/algae concentrations, as it comes from a much less developed watershed in upstate New York. On the other hand, both rivers are highly polluted but the East River has relatively lower concentrations of various water quality parameters and carries much fewer toxic industrial discharges than the Hudson River, which transverses many hundreds of miles from upstate New York. Compared with the other resources that were sampled, the rivers have the most temporal variations in levels and maybe even types of water quality parameters encountered.

Transmission spectra corresponding to water samples taken from various municipalities in New York and New Jersey are shown in Figure 1. Interpretation of these transmission spectra is made with respect to the relation

$$T(\lambda) = \frac{I_S}{I_R} \quad (2)$$



**Figure 1** | Transmission spectra for water samples taken from water systems in the New York City area for (a) wavelengths 190 to 400 nm and (b) wavelengths 400 to 1,300 nm.

where  $I_R$  and  $I_S$  are the measured transmittance of the reference sample, i.e., Type IV purified water (ASTM D1193-06), and transmittance of sample for analysis, respectively. Interpretation of spectra must consider wavelength ranges corresponding to windows of transmission, as well as windows associated with partial transmission, through an ambient water background (see [Bohren & Huffman 2004](#)).

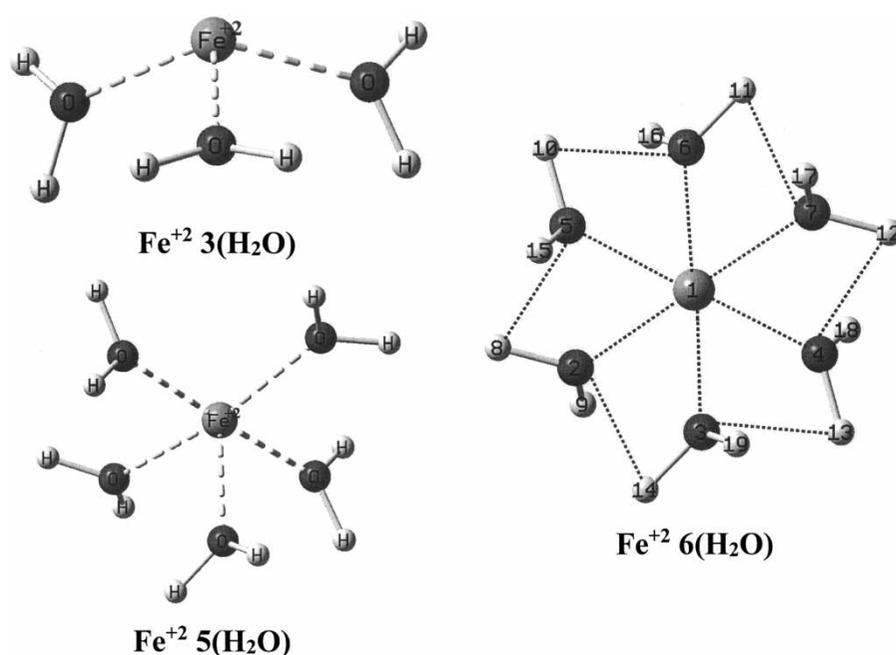
Proceeding, we first consider the transmission spectra of water samples shown in [Figure 1\(a\)](#). For these wavelengths there is essentially 100% transmission for pure water over the range of wavelengths 220 to 400 nm. Accordingly, changes in levels of transmission shown in [Figure 1\(a\)](#) can be associated with water contaminants alone.

Next, we consider the transmission spectra of water samples shown in [Figure 1\(b\)](#). For these wavelengths there is essentially 100% transmission for pure water over the range 400 to 900 nm. Accordingly, changes in levels of transmission shown in [Figure 1\(b\)](#) for these wavelengths can be associated with water contaminants alone. For the range of wavelengths 900 to 1,300 nm, we can observe absorption features associated with pure water. The relative level of absorption, however, does not dominate the transmission features associated with the water contaminants, and thus the associated range of wavelengths should still provide a sufficient window for spectral analysis of contaminants. The results of the prototype analysis shown in [Figure 1](#) demonstrate that sufficient sensitivity of hyperspectral measurements exists with respect to the characteristic variability of water contaminants as it would occur in realistic scenarios for monitoring water systems. An example of the parameterization of these hyperspectral measurements by inverse analysis is given below.

## INTERPRETATION OF SPECTRA USING BASIC THEORY

In this section an analysis of spectra using density function theory (DFT) and time-dependent-DFT (TD-DFT) is presented for the purpose of demonstrating the isolation of wavelength ranges where signature features for a specific water contaminant can be interpreted in terms of underlying molecular level interaction with electromagnetic excitation. We consider as an example of such calculations absorption spectra associated with Fe-water complexes, whose geometries are shown in [Figure 2](#). For these calculations the software GAUSSIAN09 (G09) was adopted ([Frisch \*et al.\* 2009](#)). A significant aspect of using absorption spectra calculated by DFT and TD-DFT for the physical interpretation of spectral features is that it adopts the perspective of computational physics, according to which a numerical simulation represents another source of ‘experimental’ data. This perspective is significant in that a general procedure may be developed for the physical interpretation of spectral response features using DFT and TD-DFT calculations. This type of analysis has been applied for interpretation of spectra for explosives monitoring ([Shabaev \*et al.\* 2011a, b](#); [Huang \*et al.\* 2012](#)).

For an interpretation of spectral response features correlated with Fe-water complexes, we calculate spectra using DFT and TD-DFT. The first stage of this procedure uses DFT to determine which among the many different possible Fe-water complexes are in fact stable and therefore exist. Three geometries, among the many possibilities for Fe-water complexes, that are stable energetically and therefore do have a possibility of occurrence are shown in [Figure 2](#). The second stage of the procedure entails the calculation of excitation energies and oscillator strengths for stable Fe-water complex geometries. These calculations are



**Figure 2** | Geometries of Fe-water complexes used for TD-DFT calculation of UV spectra.

given in Tables 1(a)–(c) and are of electronic excitation states within the UV range of wavelengths. Next, we note that among the three possible Fe-water complex geometries

**Table 1a** | Excitation energies and relative oscillator strengths for  $\text{Fe}^{+2} \cdot 3(\text{H}_2\text{O})$  calculated using TD-DFT

| Complex   | Excitation energy | Oscillator strength |
|---|-------------------|---------------------|
| $\text{Fe}^{+2} \cdot 3(\text{H}_2\text{O})$                  | 847.83 nm         | 0.0003              |
|   | 831.67 nm         | 0.0004              |
|   | 667.04 nm         | 0.0005              |
| $\text{Fe}^{+2} \cdot 3(\text{H}_2\text{O})$ Water Background | 1,958.26 nm       | 0.0001              |
|   | 1,560.28 nm       | 0.0001              |
|   | 762.19 nm         | 0.0002              |
|   | 707.94 nm         | 0.0002              |
|   | 641.34 nm         | 0.0003              |

**Table 1b** | Excitation energies and relative oscillator strengths for  $\text{Fe}^{+2} \cdot 5(\text{H}_2\text{O})$  calculated using TD-DFT

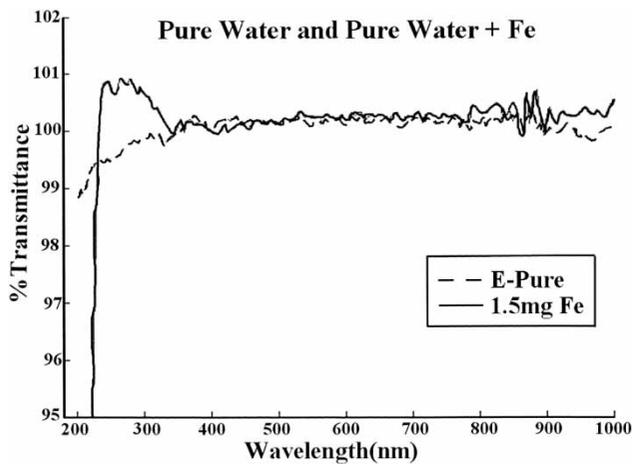
| Complex   | Excitation energy | Oscillator strength |
|---|-------------------|---------------------|
| $\text{Fe}^{+2} \cdot 5(\text{H}_2\text{O})$                  | 2,007.74 nm       | 0.0001              |
|   | 514.92 nm         | 0.0004              |
|   | 484.82 nm         | 0.0004              |
| $\text{Fe}^{+2} \cdot 5(\text{H}_2\text{O})$ Water Background | 1,473.84 nm       | 0.0002              |
|   | 1,322.75 nm       | 0.0001              |
|   | 489.22 nm         | 0.0002              |
|   | 467.55 nm         | 0.0003              |

shown in Figure 2, by far the most probable is that of  $\text{Fe}^{+2} \cdot 6(\text{H}_2\text{O})$ , for which no excitation spectra are predicted using TD-DFT for the UV and visible range of frequencies.

At this stage, we can demonstrate the use of DFT and TD-DFT for interpretation of hyperspectral signature features. Figure 3 shows transmission spectra for purified water alone, calculated according to Equation (2) for a reference transmittance corresponding to air and purified water with Fe in solution, calculated according to Equation (2) for a reference transmittance corresponding to purified water. From Figure 3 we note that for the Fe solution there is a range of wavelengths for which  $T_\lambda$  is noticeably above 100. This feature can be correlated with the presence of an increase in the relative percentage of non-absorbing scatterers in solution, i.e., the presence of  $\text{Fe}^{+2} \cdot 6(\text{H}_2\text{O})$ , in contrast to purified water, which does have absorption within the associated wavelength range, as can be seen in Figure 3.

**Table 1c** | Excitation energies and relative oscillator strengths for  $\text{Fe}^{+2} \cdot 6(\text{H}_2\text{O})$  calculated using TD-DFT

| Complex   | Excitation energy | Oscillator strength |
|---|-------------------|---------------------|
| $\text{Fe}^{+2} \cdot 6(\text{H}_2\text{O})$                  | 0.0               | 0.0                 |
| $\text{Fe}^{+2} \cdot 6(\text{H}_2\text{O})$ Water Background | 0.0               | 0.0                 |



**Figure 3** | Relative transmittance as a function of wavelength for purified water and Fe in solution (having values above 100).

## INVERSE ANALYSIS OF MEASURED SPECTRA

The mathematical foundation for inverse analysis of spectra is that of inverse scattering theory (Shubitidze & Osterberg 2007). Brown (2006) presents an inverse analysis of reflectivity measurements associated with hyperspectral imaging and detailed discussion of the methodology. A general approach for inverse analysis of spectra is the fitting of absorption spectra to a linear combination of Gaussian and Lorentian functions. This type of inverse analysis provides convenient representation of absorption bands for statistical analysis of signatures that are associated with an ensemble of spectral measurements, where there exists variability of contaminants within a restricted range of values. This type of inverse analysis enables the identification of materials that are present by comparison with library or database spectra (Brown 2006; Shubitidze & Osterberg 2007; Stancik & Brauns 2008). With respect to this type of inverse analysis, two general parametric models follow. One is given by

$$T(\nu) = \sum_{i=1}^{N_i} \alpha_i \exp \left[ \frac{(\nu - \nu_i)^2}{2\sigma_i^2} \right] \quad (3)$$

where  $T(\nu)$  is the transmission spectrum, which is recorded as a table of values, and  $\alpha_i$  is the amplitude of the  $i$ th Gaussian term, whose central frequency and full-width at half maximum are  $\nu$  and  $\sigma_i$ , respectively. Another parametric model is given by a linear combination of Lorentzian functions

$$T(\nu) = \sum_{i=1}^{N_i} \alpha_i \left[ \frac{\sigma_i}{(\nu - \nu_i)^2 + \sigma_i^2} \right] \quad (4)$$

where  $\alpha_i/\sigma_i$  is the amplitude of the  $i$ th Lorentzian term. It is significant to note that the fitting of absorption spectra to a parametric model, which is typically a linear combination of Gaussian and Lorentzian functions, represents a parametric fit to a specific hyperspectral measurement. It follows that for ensembles of hyperspectral measurements, which would be associated with a given water environment, the parameters defined with respect to Equations (3) and (4) must be generalized to represent statistical quantities. Accordingly, the sets of parameters  $(\alpha_i, \nu_i, \sigma_i)$  defined with respect to Equations (3) and (4) are to be associated with statistical distributions and thus with corresponding statistical parameters  $(\langle \alpha \rangle, \langle \nu \rangle, \langle \sigma \rangle)$ .

The model parameters defined by Equations (3) and (4) provide an optimal encoding of spectral signatures for databases that can in principle be used to characterize water systems. As an example of this type of parameter encoding we consider a prototype inverse analysis of transmission spectra for a water sample taken from the Hudson River, NYC, which is shown in Figure 1(a) for spectral window 200–400 nm. Proceeding, we obtain

$$T(\nu) = \alpha \left[ 1 - \exp \left( -\beta(\nu - \nu_1)^2 \right) \right] \quad (5)$$

where  $\alpha = 0.93$ ,  $\beta = 2.8 \times 10^{-4} \text{ (nm}^{-2}\text{)}$ ,  $\nu_1 = 213 \text{ nm}$  and  $200 < \nu < 400 \text{ nm}$ . Accordingly, the model parameters  $\alpha$ ,  $\beta$  and  $\nu_1$  defined with respect to Equation (5) are representative of database quantities for potential analysis and correlation of water system characteristics.

## CONCLUSION

The ultimate goal of the general analysis framework described here is the construction of databases for specific water resources, which can be adopted for contaminant classification algorithms. Such databases would include parametric model representations of single-additive systems (pure water with a single contaminant dissolved in it) and the archiving of the associated model-parameter values. Accordingly, in order to obtain parameter values for parametric model representations of these single-additive systems, it should be necessary to measure absorption spectra experimentally. For any given single-additive system, physical interpretation of spectral absorption features is to follow from theoretical quantum based calculations, i.e., DFT and TD-DFT. Although in practice no natural water system can be characterized by purified water with one

type of contaminant, it is expected that specific water systems can be characterized by finite ranges of contaminants, and by associated distributions of relative concentrations of these contaminants. In principle, classification can be based on minimizing the difference between estimates of model parameters obtained from specific measurements and those of a database, as well as correlation between observed trend features and those predicted using basic theory. Error tolerances for parameter estimation and the correlation of trend features with theory-based calculations remain open questions for future investigation.

A significant aspect of the general analysis framework described here is that of database verification, as well as database calibration, which would require analysis and classification of contaminants utilizing other means of classification, e.g., mass spectroscopy and chemical analysis. Knowledge of the specific range of types of contaminants, as well as their relative concentrations, would permit the determination of parametric model representations, i.e., Equations (3) and (4) for mixtures of contaminants by inverse analysis of either experimentally prepared solutions, where distributions of contaminants are quantified, or water samples from water systems of interest, whose content in terms of types and relative concentrations of contaminants are known. This information would be stored in the database for contaminant classification. Finally, in addition to contaminant classification, databases can be used for general water monitoring with respect to the detection of statistical anomalies, which would indicate the presence of a contaminant not typically present within a specific water system.

Questions concerning feasibility and sensitivity remain for the analysis framework described here. To the extent that parametric model representations (i.e. Equations (3) and (4)) and interpretation of trend features using basic theory can be used as classification metrics, it follows that classification algorithms can be developed, which draw upon libraries containing spectra, parameter estimates, as well as contaminant information obtained by other means. Ultimately, both classification algorithms and libraries can be embedded into a hyperspectral sensor system for field applications. Finally, a rational path forward for further development of the proposed methodology must examine issues concerning database size for calibration and verification, feasibility in practice, and assessment of the amount of data required to determine characteristics of water systems for classification.

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