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ISOSBESTICS IN INFRARED AEROSOL SPECTRA:
PROPOSED APPLICATIONS FOR REMOTE SENSING

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April 1989

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) CRDEC-TR-063			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION CRDEC		6b. OFFICE SYMBOL (if applicable) SMCCR-RSP-P	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION CRDEC		8b. OFFICE SYMBOL (if applicable) SMCCR-RSP-P	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423			10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO.	PROJECT NO. 1L161101	TASK NO. A91A	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Isosbestic in Infrared Aerosol Spectra: Proposed Applications for Remote Sensing					
12. PERSONAL AUTHOR(S) Carlton, Hugh R., U.S. Army Fellow					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 79 Jan TO 82 Sep		14. DATE OF REPORT (Year, Month, Day) 1989 April	15. PAGE COUNT 21
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD 17	GROUP 05	SUB-GROUP 01	Remote sensing, Infrared spectra, Aerosols, Isosbestic, Atmosphere, Rayleigh regime, Infrared, Water, (Continued on reverse)		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) When only two substances, in equilibrium with each other, are responsible for all absorption in a given wavelength region, there must exist at least one point in the spectrum where the absorption coefficient will be independent of the ratio of the concentrations of the two substances. The wavelength at which this occurs is called the isosbestic point, which is uniquely satisfactory for quantitative determinations of the amounts of the two substances present and provides an internal standard to which absorption coefficients at other wavelengths can be compared. Isosbestic points are found in many spectra of droplet aerosols, and it is shown that it should be feasible to use them for remote spectral monitoring and quantitative analyses of droplet solutions and chemical reactions if the complex indices of refraction are known. The technique seems most applicable in the Rayleigh regime.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL SANDRA J. JOHNSON			22b. TELEPHONE (Include Area Code) (301) 671-2914	22c. OFFICE SYMBOL SMCCR-SPS-T	

UNCLASSIFIED

18. Subject Terms (Continued)

Solutes	Optical scattering
H ₃ PO ₄	Isosbestic points

PREFACE

The work described in this report was authorized under Project No. 1L161101A91A, In-House Laboratory Independent Research (ILIR) from January 1979 through September 1982.

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Acknowledgment

Data from Reference 3 were tabulated and plotted for the figures in this report by Robert H. Frickel, who also provided data and discussion relating to Reference 7; his assistance is sincerely appreciated.

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**ISOSBESTICS IN INFRARED AEROSOL SPECTRA:
PROPOSED APPLICATIONS FOR REMOTE SENSING**

1. INTRODUCTION

When only two substances, in equilibrium with each other, are responsible for all absorption in a given wavelength region, it is easily shown¹ that there must exist at least one point in the spectrum where the absorption coefficient will be independent of the ratio of the concentrations of the two substances. The wavelength at which this occurs is called the isosbestic point or, sometimes, the isobestic point. The absence of an isosbestic point is definite proof of the presence of a third constituent, if it can be assumed that the Beer-Lambert law is applicable:

$$\ln(1/T_\lambda) = \alpha_\lambda CL, \quad (1)$$

where T_λ is the optical transmittance at wavelength λ (μm), α_λ is the mass extinction coefficient (m^2/g), C in this paper is the aerosol mass concentration (g/m^3), and L is the optical pathlength (m). Bauman¹ has given an interesting discussion of isosbestics and of isosbestic points.

The existence of an isosbestic point is not proof of the presence of only two substances, since other substances might very well have zero absorptivity at a particular wavelength. But when present, an isosbestic point provides a uniquely satisfactory wavelength for quantitative determinations of the total amounts of the two absorbing substances present. The isosbestic wavelength may also provide a convenient reference point, or internal standard, to which the absorption coefficient of one or the other substances may be referred in order to find the ratio of the amounts present.

At an isosbestic wavelength, total absorption is dependent only on the total number of chemical equivalents of the two substances, without regard to the equilibrium position of the reaction between them. Since any determination of the number of chemical equivalents present in a solution implies a knowledge of the chemical valences of the substances, one also obtains clues as to what species might be present in unknown solutions whose spectra contain isosbestic points. Isosbestic-like points also are observed in spectra of pure liquid water for samples subjected to large variations in temperature.²

2. AEROSOL EXTINCTION

This paper considers isosbestic behavior in liquid solutions which are dispersed as droplet aerosols in the atmosphere and whose spectra are observed in the infrared. Thus, in addition to absorption by the droplets,

one must also consider optical scattering which contributes to the aerosol extinction coefficient, α_λ , and is dependent upon the real part of the complex index of refraction and upon droplet diameter. An excellent example is found in the droplet aerosols (smokes) which are produced by burning phosphorus. Querry and his co-workers³ recently have completed measurements of the complex indices of refraction for several representative concentrations of acid solutions comprising these smokes, including samples for 5, 10, 20, 40, 50, 65, 75 and 85% by weight orthophosphoric acid (H_3PO_4).

While the real part of the complex index of refraction ("real index") does not fit the definition given at the beginning of this paper, isosbestic-like points nonetheless occur in the real index and their spectra will be discussed briefly with those of the imaginary index in this paper. Experimental spectra for phosphorus smokes have been reported previously.⁴ Although it is now known that such smokes contain phosphorus compounds not limited only to H_3PO_4 , the optical constants from Reference 3 are typical of those for many water-based acid smokes and they exhibit isosbestic points.

Figures 1 and 2 show the real part of the index of refraction, n_λ , measured by Querry et al,³ for several acid concentrations versus wavelength λ for the spectral intervals 2-6 μm and 6-16 μm , respectively. Isosbestic-like wavelengths for n_λ can be seen near $\lambda = 2.95, 3.6, 7.1$ and $9.7 \mu m$. Figures 3 and 4 show the imaginary part, k_λ , of the complex index of refraction $(n - ik)_\lambda$ from Reference 3 for the same acid concentrations and spectral intervals. Isosbestic wavelengths for k_λ can be seen near $\lambda = 3.2$ and $12.5 \mu m$.

Also included in Figures 1-4 are curves for the refractive indices of pure water, which can be considered as the ultimate dilution case for these phosphorus smokes. When acid smokes exist in moist atmospheres, complex interactions occur between the individual droplets and the water vapor that surrounds them. The equilibria are such that the droplet size distribution is directly proportional to humidity, and thus, the acid concentration of the droplets is inversely proportional to humidity.

The curves in Figures 1-4 can be used to represent spectra of orthophosphoric acid droplets formed by burning phosphorus under conditions ranging from very dry air (resulting in 85% acid droplets) to very moist air near saturation (resulting in droplets containing only traces of acid). These curves would represent a very wide range of solute concentrations and wavelengths for these atmospheric aerosols. Not all solute concentration curves are shown in all figures.

The Mie theory^{5,6} gives the value of the extinction coefficient for spherical-droplet aerosols as:

$$\alpha_\lambda = 3Q_\lambda/2D_\mu\rho, \quad (2)$$

INDEX OF REFRACTION OF H_3PO_4 (REAL PART)

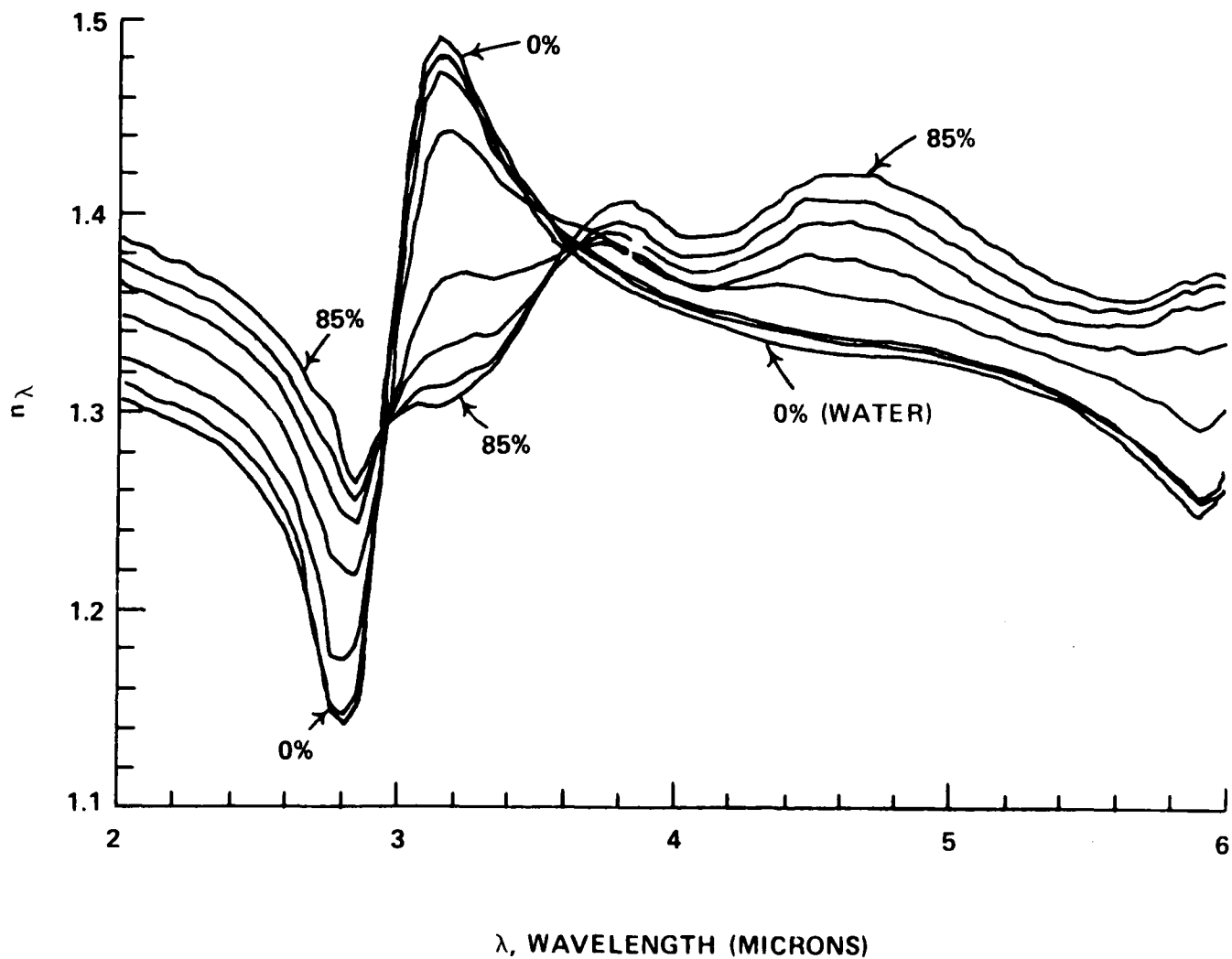


Figure 1. Real Part, n_λ , of the Complex Index of Refraction for Several Concentrations of Orthophosphoric Acid (H_3PO_4) in Water, 2-6 μm Wavelength Interval (Ref. 3).

INDEX OF REFRACTION OF H_3PO_4 (REAL PART)

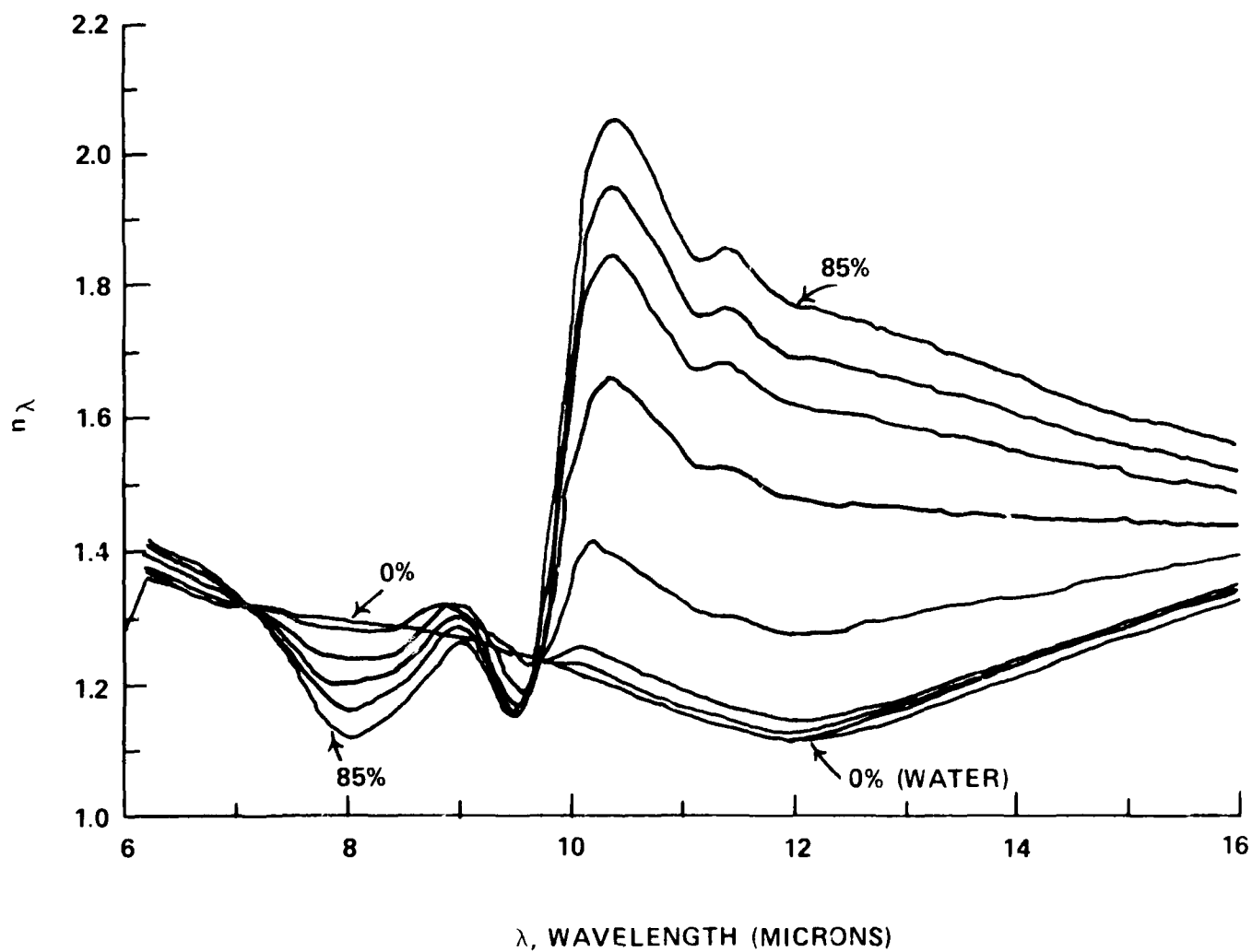


Figure 2. Real Part, n_λ , of the Complex Index of Refraction for Several Concentrations of Orthophosphoric Acid (H_3PO_4) in Water, 6-16 μm Wavelength Interval (Ref. 3).

INDEX OF REFRACTION OF H_3PO_4 (IMAGINARY PART)

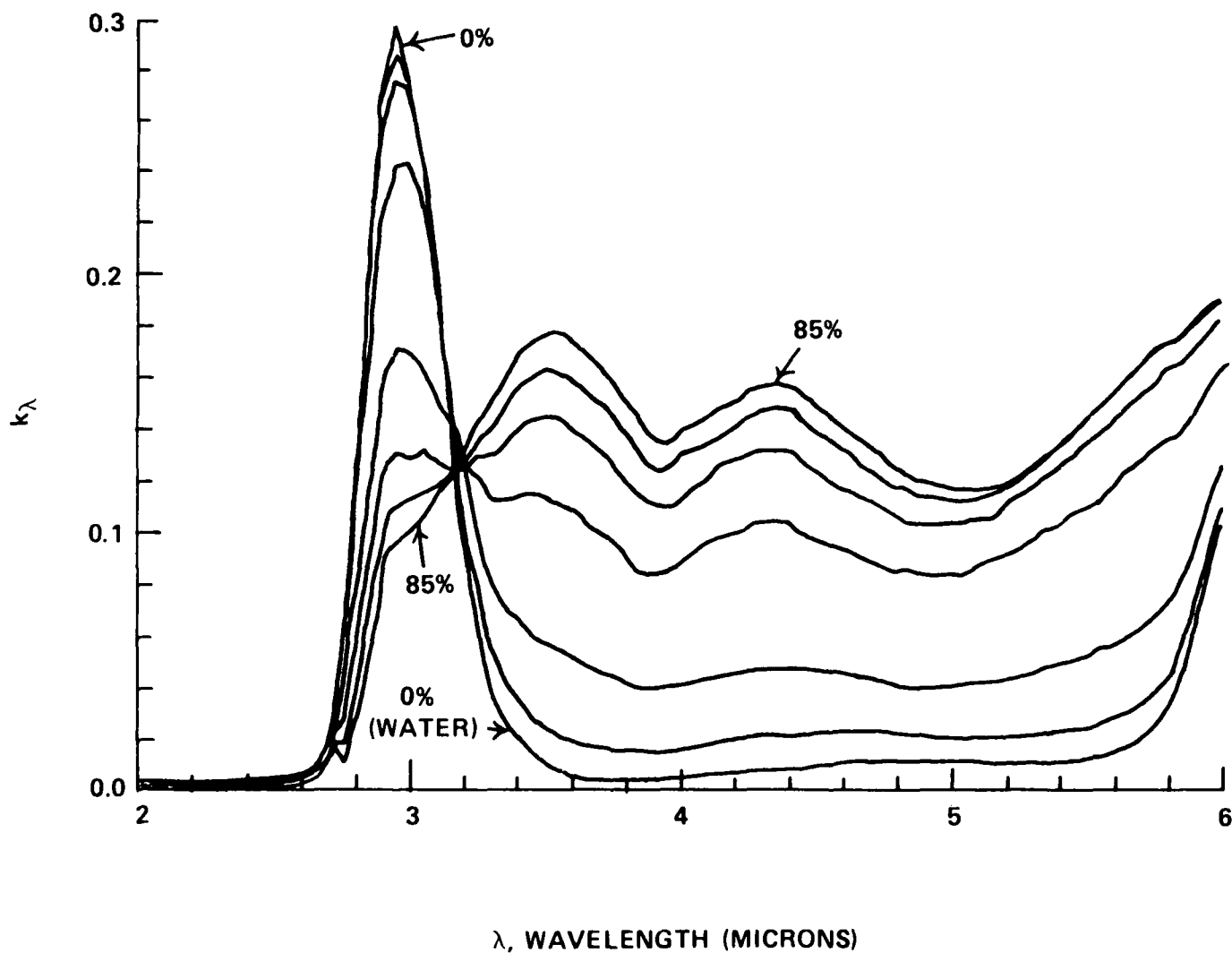


Figure 3. Imaginary Part, k_λ , of the Complex Index of Refraction for Several Concentrations of Orthophosphoric Acid (H_3PO_4) in Water, 2-6 μm Wavelength Interval (Ref. 3).

INDEX OF REFRACTION OF H_3PO_4 (IMAGINARY PART)

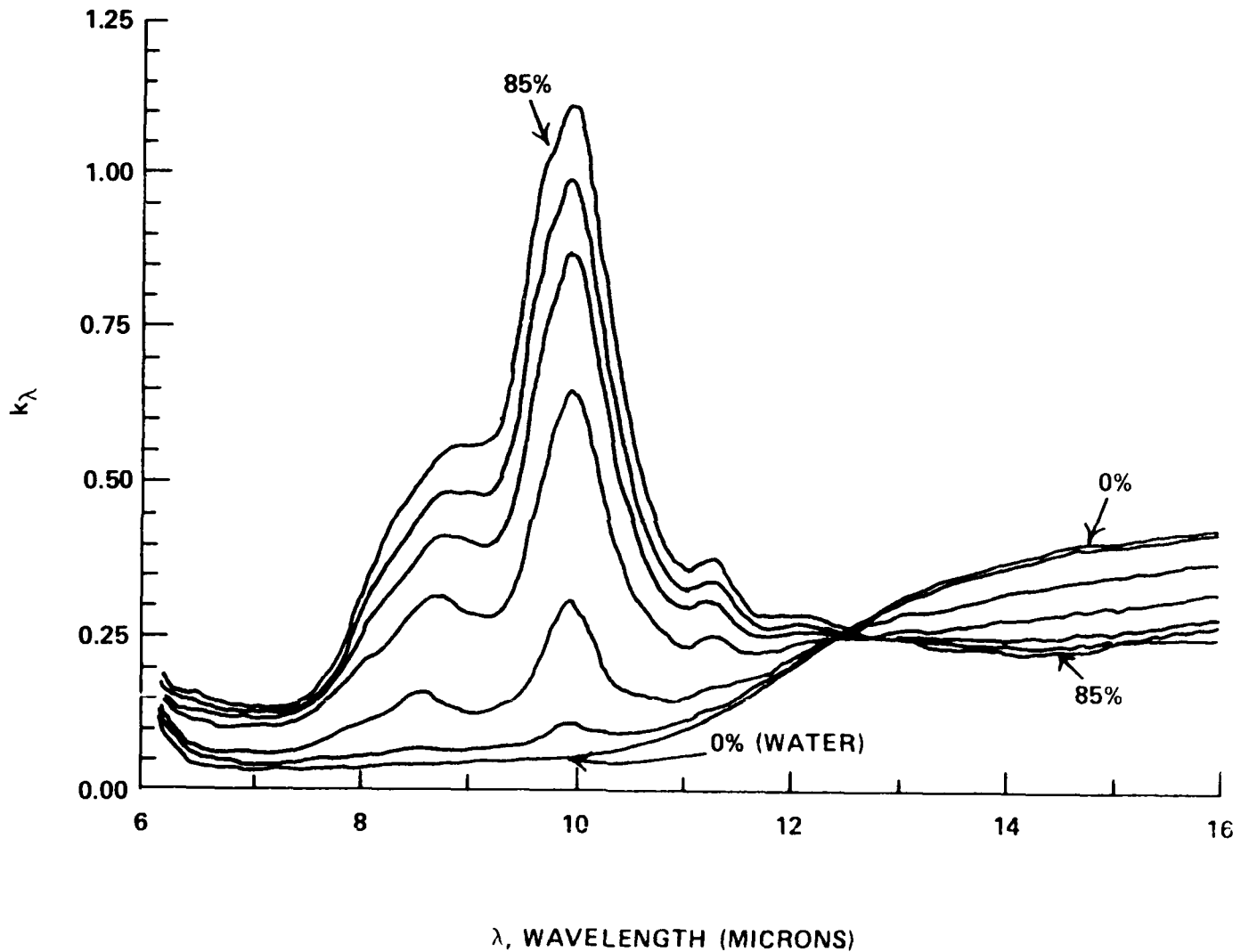


Figure 4. Imaginary Part, k_λ , of the Complex Index of Refraction for Several Concentrations of Orthophosphoric Acid (H_3PO_4) in Water, 6-16 μm Wavelength Interval (Ref. 3).

where D_μ is the droplet diameter in μm and ρ is the droplet mass density, grams per cubic centimeter³. Q_λ is a cross-section efficiency factor that is the sum of two factors, $Q_{S\lambda}$, which is the optical scattering efficiency and is related to n_λ and k_λ , and $Q_{A\lambda}$, which is the absorption efficiency and is closely related to k_λ . Thus, if λ is the wavelength in micrometers

$$Q_\lambda = Q_{S\lambda} + Q_{A\lambda} \quad (3)$$

Because of these relationships, it would be expected that at any wavelength where an isosbestic-like point is found in spectra of n_λ (Figures 1 and 2), $Q_{S\lambda}$ should remain relatively constant compared to $Q_{A\lambda}$ which would in turn control Q_λ (Equation (3)), and thus the aerosol mass extinction coefficient in meters squared per gram, α_λ (Equation (2)). Conversely, at any wavelength where an isosbestic point is found in spectra of k_λ (Figures 3 and 4), $Q_{A\lambda}$ should remain relatively constant compared to $Q_{S\lambda}$ which would control Q_λ and thus α_λ .

In the first case, the aerosol extinction coefficient should be determined primarily by droplet absorption, while in the second case it should depend mostly on droplet scattering. Actual extinction coefficient (α_λ) spectra⁷ calculated from the Mie theory for values of n_λ and k_λ in Figures 1-4 are shown for somewhat narrower wavelength intervals in Figures 5 and 6. It can be seen that the values of α_λ and hence of Q_λ (Equations (2) and (3)) show the general trends just discussed.

3. DISCUSSION AND PROPOSED APPLICATIONS

Figure 6 shows that there is a well-defined isosbestic point in the extinction coefficient spectra of phosphoric acid droplet clouds at $\lambda = 11.4 \mu\text{m}$ where $\alpha_{11.4}$ is approximately 0.13-0.15 and is nearly constant over a wide range of droplet solute concentrations. The figure shows that this decidedly is not true at other wavelengths except near $\lambda = 7 \mu\text{m}$ where the curves approach each other. Most phosphoric acid droplets have diameters, D_μ , much smaller than the IR wavelengths considered here (D_μ is much smaller than λ), so that they exist in the Rayleigh regime⁶ where:

$$\alpha_\lambda \approx 4\pi k_\lambda f(m_\lambda) / \lambda \rho \quad (4)$$

and

$$f(m_\lambda) = \frac{9n_\lambda}{(n_\lambda^2 + k_\lambda^2)^2 + 4(n_\lambda^2 - k_\lambda^2) + 4} \quad (5)$$

Thus, $\alpha_{11.4}$ is approximately 0.13-0.15 because, e.g., for water or very dilute acid droplets, $k_{11.4} = 0.125$ (Figure 4) at the isosbestic wavelength (11.4 μm), and from Equation (4), $\alpha_{11.4}$ is approximately equal to $4\pi(0.125)(0.95)/(11.4)(1.0)$ or $0.13 \text{ m}^2/\text{g}$ where $f(m_{11.4}) = 0.95$ (Equation (5) and Figures 2 and 4) and $\rho = 1.0$.

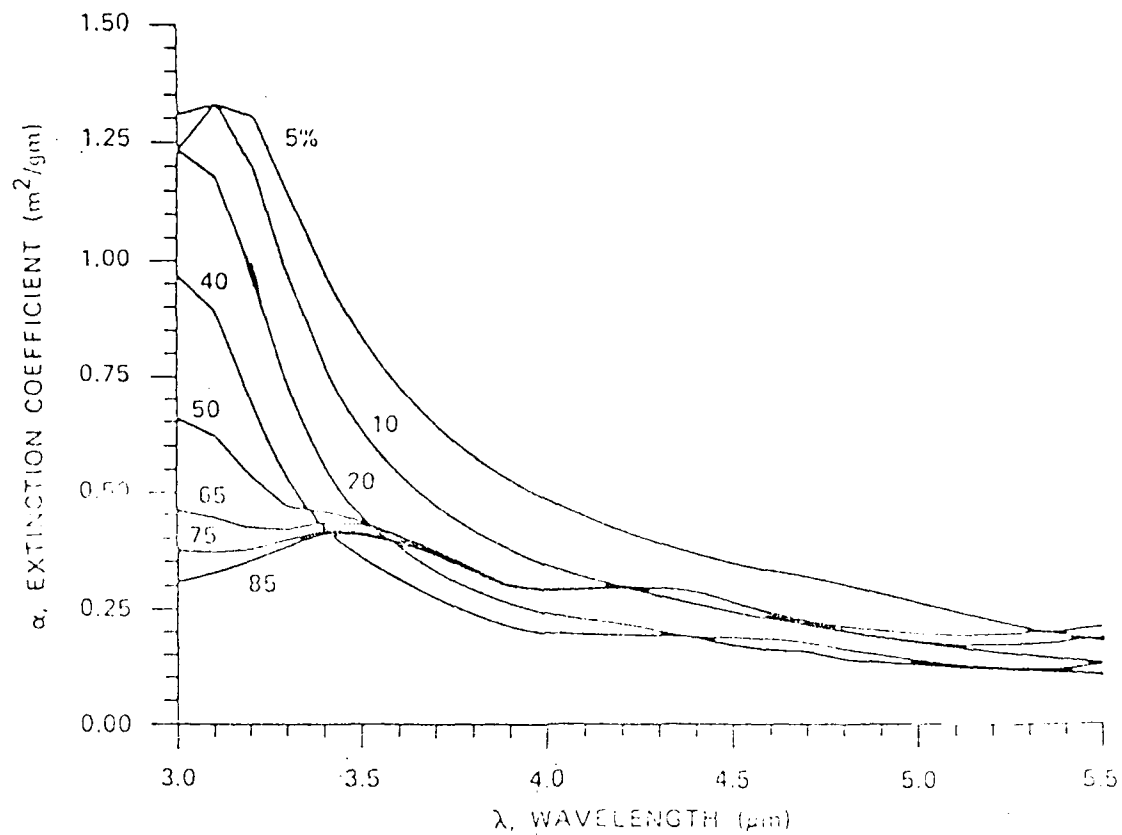


Figure 5. Computed Extinction Coefficient (α_λ) Spectra for Liquid Droplet Aerosols Comprising Several Concentrations of Orthophosphoric Acid (H_3PO_4) in water, 3.0-5.5 μm Wavelength Interval (Refs. 3 and 7).

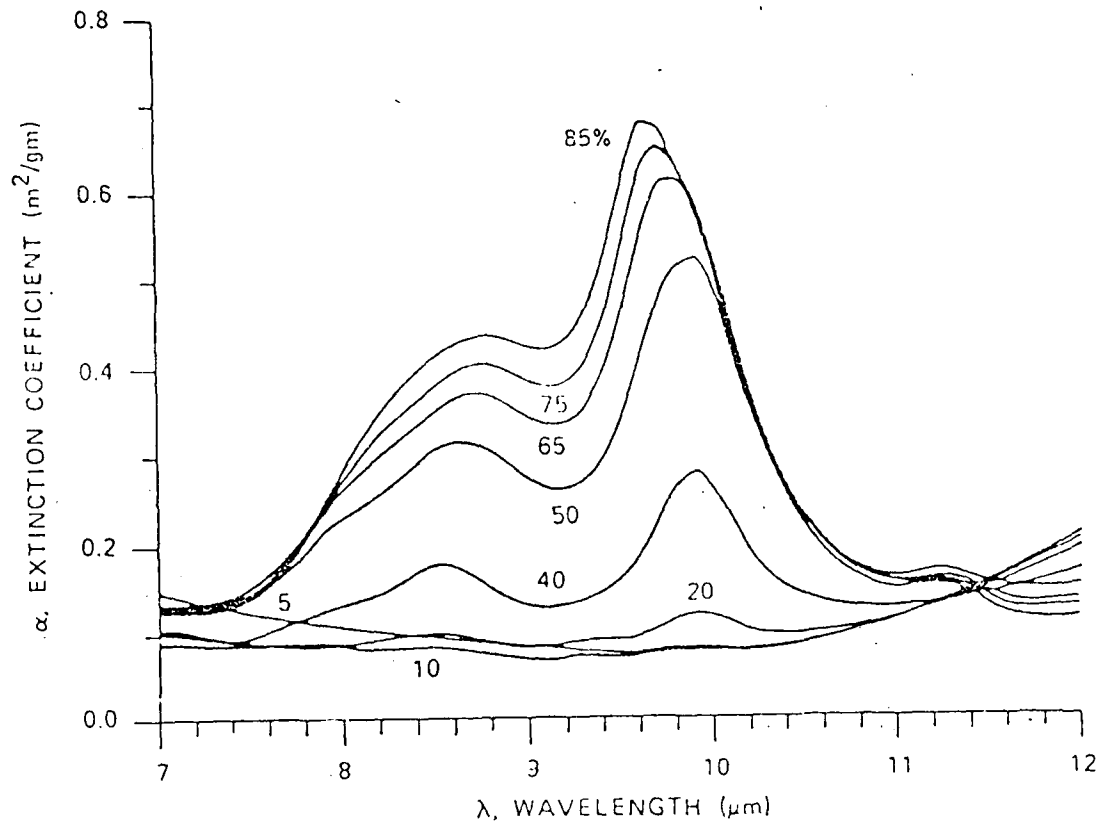


Figure 6. Computed Extinction Coefficient (α_λ) Spectra for Liquid Droplet Aerosols Comprising Several Concentrations of Orthophosphoric Acid (H_3PO_4) in water, 7-12 μm Wavelength Interval (Refs. 3 and 7).

In discussing possible applications of isosbestic in the spectrometry of aerosols, one must proceed with caution. The technique represents a significant extrapolation of what is known for liquid solutions as discussed by Bauman.¹ The implications are fairly obvious. If the mass extinction coefficient of an aerosol remains constant at some isosbestic wavelength, regardless of the solute/water ratio, it should be possible to monitor this wavelength. Simultaneously, a second wavelength where the extinction (absorption) coefficient versus solute concentration is known can be monitored to perform remote quantitative analyses of such aerosols.

This should be simplest in the Rayleigh regime, where particles are much smaller than the observation wavelengths and scattering contributes little to the extinction coefficients. Such a case was stated to exist for phosphorus smokes in the 8-13 μm IR window region.⁴ Nevertheless, one must deal with the complications that are introduced due to complex scattering effects in spherical-droplet aerosols.⁵ These effects can produce ambiguities that do not exist in the spectrometry of liquid films as described by Bauman.

Again, consider the isosbestic point for the extinction coefficient of H_3PO_4 at $\lambda = 11.4 \mu\text{m}$ (Figure 6). Since the mean particle diameter for a typical phosphoric acid smoke is about $1 \mu\text{m}$ (Reference 4) and the condition $D_p \ll \lambda$ is much smaller than $\lambda = 11.4 \mu\text{m}$ exists, Equations (4) and (5) apply. It has already been shown that for these conditions α_λ can be calculated at the isosbestic point ($\lambda = 11.4 \mu\text{m}$).

Suppose that one wished to monitor the aerosol solute (acid) concentration remotely by simultaneous observations at $\lambda = 11.4 \mu\text{m}$ and at $\lambda = 9.7 \mu\text{m}$ where a strong acid absorption peak occurs, and $\alpha_{9.7}$ (Figure 6) is very dependent upon the droplet acid concentrations. Presumably transmittances would be measured for the same optical path through the same aerosol cloud. Thus Equations (1) and (4) can be combined to give:

$$\frac{\lambda \ln (1/T_\lambda)}{k_\lambda f(m_\lambda)} = \frac{4\pi C L}{\rho} \quad (6)$$

where the right-hand terms are constants or are common to the aerosol cloud for either transmittance reading. The term $f(m_\lambda)$ depends only on the complex index of refraction and is given by Equation (5). Thus, the left-hand side of Equation (6) can be written for two wavelengths and set equal so that:

$$\frac{\ln T_2}{\ln T_1} = \frac{k_2 \lambda_1 f(m_2)}{k_1 \lambda_2 f(m_1)} \quad (7)$$

Of course, Equation (7) could be used for any two wavelengths. But when one, say λ_1 , is an isosbestic point, then α_1 is a constant and since

$$\ln (1/T_1) = \alpha_1 CL \quad (8)$$

it becomes possible to solve for k_2 at λ_2 because

$$\frac{\ln T_2}{\ln T_1} = \frac{4\pi k_2 f(m_2)}{\alpha_1 \rho_2 \lambda_2} \quad (9)$$

Quantitative analysis of the aerosol then is accomplished by comparing calculated values of k_2 to values previously determined for various solute concentrations at λ_2 , that is as in Figure 4 in the Rayleigh regime. α_2 of the aerosol is known directly because

$$\frac{\ln T_2}{\ln T_1} = \frac{\alpha_2}{\alpha_1} \quad (10)$$

and α_2 can also be compared to known mass extinction coefficient spectra for the aerosols under observation.

For many common droplet aerosols (such as water fogs), the value of $f(m_\lambda)$ is approximately 1.0 in the Rayleigh regime where D_μ is much smaller than λ , and Equation (7) or (9) would seem to give unambiguous results. But with a solute present in the droplets, the results are not so clear cut because $f(m_\lambda)$ depends upon the complex index of refraction for various solute (that is, phosphoric acid) concentrations.

Actual results calculated from Figures 2 and 4 for $\lambda_1 = 11.4 \mu\text{m}$ and $\lambda_2 = 9.7 \mu\text{m}$ are given in Table 1. The table shows that monitoring of droplet solute concentration by using the $9.7 \mu\text{m}$ wavelength referenced to $11.4 \mu\text{m}$ should be possible. Because of the deviation of $f(m_\lambda)$ from a value near unity especially for large solute concentrations, some calculations have to be performed by trial and error using Figures 2 and 4 and Equations (7) or (9), if precision is desired.

In the absence of isosbestic, standard aerosols of known solute concentrations (and droplet sizes, if applicable) could be used with Equation (10) to calibrate a transmissometer to be used to monitor aerosol-phase reactions, for example, in industrial processes. The use of an isosbestic or reference wavelength with a second, absorption-dependent wavelength, to remotely monitor solute concentrations or chemical reactions in droplet aerosols appears feasible. This seems possible even for aerosols for which $f(m_\lambda)$ is not unity but for which complex indices of refraction are known as functions of the monitored solution activity at the selected wavelengths.

Table 1. Data and Calculated Values for Phosphorus Smokes

Solute (acid) Concentration in Aerosol Droplets	0% (Water)	50%	85%
$k_{11.4}$	0.125	0.23	0.32
$n_{11.4}$	1.14	1.51	1.85
$f(m_{11.4})$	0.95	0.74	0.56
$k_{9.7}$	0.05	0.50	1.02
$n_{9.7}$	1.24	1.24	1.24
$f(m_{9.7})$	0.89	0.90	0.73
K	2.43	0.36	0.27

Where: $\ln(T_{11.4}) = K \ln(T_{9.7})$

4. CONCLUSIONS

Isosbestic points (wavelengths) are found in many spectra of atmospheric liquid droplet aerosols. When they occur, mass extinction coefficients of aerosols at these wavelengths are remarkably independent of droplet solute concentration, temperature, and often even particle size or distribution.

Thus isosbestic points appear to be useful in remote sensing and monitoring of solution or chemical reactions in droplet aerosols if the complex indices of refraction or droplet extinction data are known. An isosbestic point can serve as a reference for optical transmittance against which transmittances at other wavelengths can be compared to monitor appropriate activity. The technique seems most applicable in the Rayleigh regime.

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