burn fuel oil representing a single geographic and geologic crude source. It does, however, point to the possibility of identifying other industrial sources through some unique or characteristic particle composition where this identification would be lost in a total analysis of a gross particle collection. Such studies at the single particle level would be of great help in isolating and eventually controlling sources of inorganic particulate or aerosol pollutants detrimental to both health and the environment.

Anomalous Absorption Bands in Ultraviolet Spectra of Halide Solutions

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Selective absorptions at 270, 302, and 357 nm due to $PbCl_6^{4-}$, $PbBr_6^{4-}$, and PbI_6^{4-}, respectively, are responsible for the absorptions observed by some early workers investigating the ultraviolet spectra of concentrated aqueous solutions of metal halides. The reports of these workers conflict with those of others who find no discrete absorptions in this region. Evidence is presented that implicates lead-containing solder glass used in the construction of their sample holding vessels as the probable source of the lead contamination.

RECENTLY, IN THE TAKING of spectra of relatively concentrated aqueous halide solutions, unexpected strong absorptions appeared at definite wavelengths in the ultraviolet region. The exact position of the absorption maximum depended upon the nature and concentration of the halide anion involved. Further investigation indicated that these absorptions would be observed only if the halide solution were contained in certain of the silica glass cuvettes available in our laboratory. The identification of the absorbing species and the resolving of the conflicting reports in the literature regarding the spectra of aqueous halide solutions are the concern of this paper.

A marked absence of agreement exists in the literature of UV spectral absorptions of aqueous solutions of both hydrohalic acids and their salts as reported by a dozen or more investigators during the first third of this century. Some of the earlier workers found the UV spectra of the solutions to be more or less transparent in the mid-UV region in some cases, whereas others found a generally increasing absorption with decreasing wavelength. However, most of the investigators have reported observing a selective absorption, *i.e.*, an absorption maximum, at a wavelength that appeared to be characteristic for the halide involved. The literature does not indicate that the disharmonious nature of these reports has ever been resolved. Table I lists the authors and their observations (*1–17*).

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EXPERIMENTAL

Solutions for these spectral scans were prepared from chemicals available in this laboratory and, for the most part, were of analytical reagent grade. The solid salts and liquid acid solutions were used without further purification. All solutions were intended to be saturated but no special equipment was used or analyses taken to ensure saturation. Distilled water was used in the preparations of the solutions and in all ensuing dilutions.

For solutions containing known Pb^{2+} concentrations, a stock solution of $10^{-3}M$ lead nitrate was prepared. A series of lead-halide mixtures for spectral measurements were prepared in 10-ml quantities; 1 ml of the Pb^{2+} solution was mixed with 9 ml of a saturated halide solution, 2 ml of the Pb^{2+} solution with 8 ml of the halide, etc., until precipitation of the insoluble PbX_2 occurred.

All spectra were run on a Beckman DK-2A Ratio Recording Spectrophotometer using Beckman Standard Silica (blue label), Beckman Near Infrared Silica (red label) cuvettes as well as a number of others of unknown origin.

RESULTS

Concentrated solutions of analytical reagent grade chlorides of H, Li, Na, K, NH_4, Mg, Ca, and Sr are transparent in the UV region down to about 230–240 nm if the spectra of the solutions are scanned in certain cuvettes. These cuvettes do not interact with the sample solutions and are referred to as being "inactive."

However, these same solutions remaining in other cells for relatively short periods (a few minutes to a few hours) will produce an absorption whose maximum is at 270 nm. These "active" cells apparently do react with the halide samples. The cation apparently has no significant effect upon the absorption other than to affect the solubilities of the salts.

(1) P. J. Brannigan and A. K. Macbeth, *J. Chem. Soc., London*, **109**, 1277 (1916).
(2) G. M. Pool, *Z. Phys.*, **29**, 311 (1924).
(3) F. H. Getman, *J. Phys. Chem.*, **29**, 853 (1925).
(4) G. F. Hüttig and M. Keller, *Z. Electrochem.*, **31**, 390 (1925).
(5) A. Hantzsch, *Ber. Deut. Chem. Gesell.*, **59**, 1096 (1926).
(6) E. Viterbi, *Gazz. Chim. Ital.*, **57**, 615 (1927).
(7) L. A. Müller, *Ann. Phys.*, **82**, 39 (1927).
(8) G. F. Hüttig and H. Kükenthal, *Z. Electrochem.*, **34**, 14 (1928).

(9) J. von Koczkas, *Z. Phys.*, **59**, 274 (1929).
(10) *Ibid.*, **61**, 545 (1930).
(11) H. Fromherz and W. Menschick, *Z. Phys. Chem., Abt. B*, **7**, 439 (1930).
(12) V. Henri and N. Desmaissieux, *C. R. Acad. Sci.*, **193**, 591 (1931).
(13) R. Trehin, *ibid.*, **191**, 774 (1930).
(14) *Ibid.*, **193**, 1089 (1931).
(15) *Ibid.*, **195**, 1269 (1932).
(16) *Ibid.*, **199**, 1047 (1934).
(17) R. Trehin, *J. Phys. Rad.*, **4**, 440 (1933); *Chem. Abstr.*, **27**, 5646 (1933).

Table I. Ultraviolet Spectra of Aqueous Halide Solutions as Reported in the Literature[a]

	Brannigan & Macbeth (1)	Pool (2)	Getman (3)	Hüttig & Keller (4)	Hantzsch (5)	Viterbi (6)	Müller (7)	Hüttig & Kükenthal (8)	von Koczkas	Fromherz & Menschick (11)	Henri (12)	Trehin
HCl	268.0				c			b	281.9 (9)		e	b (13, 15, 17)
LiCl	268.0			270					270.2 (9)	272		b (14)
NaCl	268.0				d		b					b (14)
KCl							b					b (14)
RbCl	268.0						b			272		
CsCl							296.6			273		
MgCl₂		270.0	274						275.0 (9)			b (16)
CaCl₂		270.0	273			271.5			270.0 (10) 269.4 (9)			b (16)
SrCl₂		279.2	274			266.5			270.0 (10) 269.8 (9)			b (16)
BaCl₂		269.0 264.4 256.0	b			262.4			270.0 (10) 269.1 (9)			b (16)
MnCl₂									406.0 (9) 362.3 270.2			
CoCl₂									b (10)			
ZnCl₂			273						b (10)			
AlCl₃			260						b (10)			
NiCl₂									b (10)			
CdCl₂			b						b (10)			
HgCl₂			b									
CuCl₂			b									
HBr					c							
LiBr				269 300						303		
NaBr	280.0				b		b					
KBr	280.0						b					
RbBr							b					
CsBr							b					
NH₄Br	280.0											
HI					c							
LiI	356.7		360							359		
NaI	356.7						315.3			354		
KI	356.7				b		b			353		
RbI	356.7						324.5					
CsI	356.7											
NaF							b					
KF							b					

[a] Numerical values indicate λ_{max} (nm) of selective absorptions observed.
[b] No selective absorption observed; a generally increasing absorption with decreasing wavelength.
[c] No selective absorption observed.
[d] No selective absorption near 270 nm observed.
[e] Transparent down to 214 nm.

Similarly, bromides and iodides also produce characteristic selective absorptions in the UV when stored in the active cuvettes for short intervals of time, whereas they are transparent in the same region if the spectra are observed with the solutions in inactive cuvettes. The characteristic λ_{max} for concentrated bromide solutions of H, Li, Na, K, and NH₄ is 302 nm and that of concentrated iodide solutions of H, Li, Na, and K is 357 nm.

A halide complex of a metal or metalloid atom was suspected as the absorber. Initially, it was hypothesized that silicon was the element most likely to be leached from the cuvette material to produce an absorbing species analogous to the SiF_6^{2-} anion. However, no conclusive evidence for the existence of this species in solution could be found.

Unlike the listed cations above, halide solutions containing copper do absorb selectively when scanned in "inactive" cuvettes and the λ_{max}, in the instance of the chloride and the iodide, correspond quite closely to those obtained from the

same halide solutions scanned in "active" cells. The bromide solution, however, produces a peak at 275 nm as compared to 302 nm obtained from bromide solutions in active cuvettes and thus confirms that copper is not the element abstracted from the body of the cuvette.

In a manner similar to copper, concentrated halide solutions containing very small concentrations of Pb^{2+} ions (10^{-4}–$10^{-3}M$) also absorb selectively in the UV region. The position of the absorption maximum again depends upon the halide involved. The chloride, bromide, and iodide absorptions occur at 270, 302, and 357 nm, respectively.

These same absorptions are also easily obtained merely by stirring concentrated halide solutions for a few seconds with a freshly scraped piece of sheet lead.

Dilution of the concentrated halide solutions containing traces of lead with distilled water repositions the λ_{max} farther into the UV region. However, dilution of the lead-containing halide solutions with saturated lead-free halide solution causes
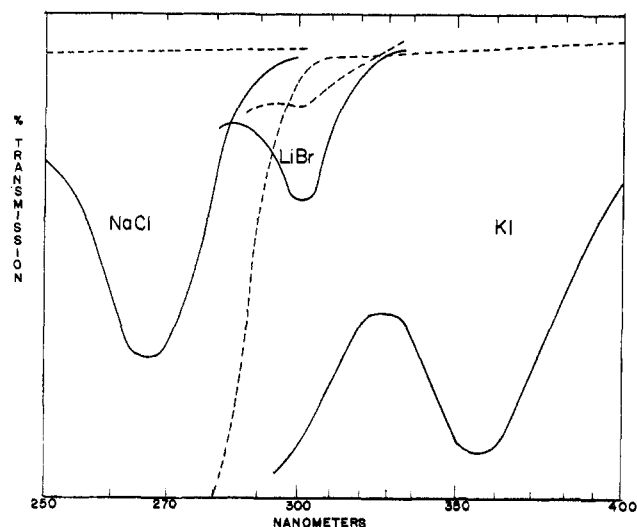
Figure 1. Absorption curves of concentrated halide solutions before (dashed lines) and after (solid lines) contact with active cuvettes
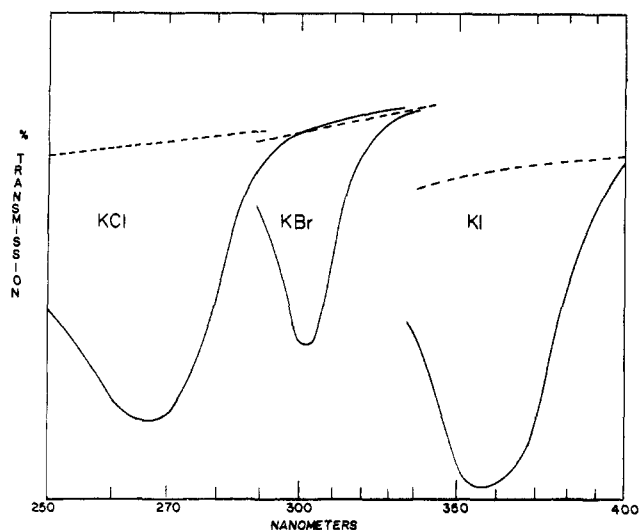

Figure 2. Absorption curves of concentrated halide solutions (dashed lines). Same solutions containing low concentrations of Pb^{2+} ions (dashed lines)

a diminution of the absorbance but produces no displacement of λ_{max}.

Equilibrating a solution of KI that produces an absorption at 357 nm with an excess of AgCl results in a solution that no longer absorbs at 357 nm but possesses, instead, a new absorption at 270 nm. A control solution of KI with no 357-nm absorption produces no 270-nm peak when treated in a similar way.

If a solution of NaCl with an absorption at 270 nm is evaporated to dryness in a Pt crucible and indeed, even further heated to fusion, the residue, when cooled and reconstituted with distilled water to the original volume, produces the same absorption. A solution of HCl with the same absorption does not show the absorption when evaporated to dryness and then brought back to its original volume with water.

It is noted that, for the halide series consisting of Cl, Br, and I, the wavelengths of the absorption maxima decrease with decreasing atomic weight of the halide atom. The fluoride ion might be expected to produce an absorption in

the region below 270 nm when a small concentration of lead is present. Such an absorption was not observed in concentrated KF solutions in contact with an "active" cell nor in those solutions containing a small amount of lead.

Figure 1 shows the absorptions of chlorides, bromides, and iodides in "inactive" cuvettes (dashed lines) and the selective absorptions of the same halides after contact with "active" cuvettes.

Figure 2 emphasizes the similarity of both the general forms of the spectra of halide solutions containing low concentrations of lead to those in Figure 1. The λ_{max} of these absorptions are essentially identical to those in Figure 1.

DISCUSSION

That the three characteristic absorptions observed at 270, 302, and 357 nm in the cases of halide solutions in contact with "active" cells are not due to the halide ion itself was demonstrated by the absence of absorptions at these wavelengths in the cases of similar halide solutions in contact with "inactive" cells. The continuing increase of absorbance at the characteristic wavelengths with time of contact indicates also the existence of a progressive process. In both the maxima and the general shapes of the absorptions, the halide solutions containing traces of lead appear identical to those observed in halide solutions exposed to the "active" cells.

The complex anionic absorber, $PbCl_6^{4-}$, has been recently described by Haight and Petersen (18) and its absorption at 270 nm has been assigned to the ligand-to-metal charge transfer band of this species. The anion $PbBr_6^{4-}$ absorbs at 302 nm according to the observation of Nilsson and Haight (19). The similarity of these maxima to those observed in this work suggests that the assignment of the absorption at 357 nm to PbI_6^{4-} is a reasonable extension of the series.

Our observation that absorbing chloride solutions diluted with water experience a shift of λ_{max} to smaller wavelengths whereas dilution with a concentrated halide solution (of the same species) merely diminishes the absorbance is consistent with the findings of Haight and Petersen (18), indicating that six is the maximum coordination number possible for the chloro complexes of lead and that $PbCl_6^{4-}$ is the predominant species in concentrated chloride solutions. Equilibria exist among $PbCl_6^{4-}$ and the chloro-lead complexes of lower coordination number. The latter, favored in more dilute solutions, are the cause of a general hypsochromic shift of the absorption peak.

In view of the extreme similarity between the spectral absorptions observed by some of the earlier workers and those reported in this work, it appears highly probable that some of the earlier investigators measured the spectra of carefully purified halide solutions inadvertently contaminated with low concentrations of lead.

To be useful in the UV range, cuvettes are made of fused quartz or 96% silica glass. Fabrication of the cell is facilitated by use of solder glass to join the faces of the cuvette. Solder glass, a low melting glass of varying formulations, commonly contains lead salts to produce its useful property.

Thus, in the work done several decades ago as in this case, it appears that, when cells made with leaded solder glass were used as sample-holding vessels, lead leached into the halide solutions producing small concentrations of highly absorbing lead complexes. Absorptivity values of 20750 cm^{-1} M^{-1} for

(18) G. P. Haight and J. R. Petersen, Inorg. Chem., 4, 1073 (1965).
(19) L. Nilsson and G. P. Haight, Acta Chem. Scand., 20, 486 (1966).

PbBr$_6$$^{4-}$ and 14910 cm^{-1} M^{-1} for PbCl$_6$$^{4-}$ have been reported (*19*).

Cuvettes that were not made with lead-containing solder glass did not cause the formation of these complexes and their spectra did not show selective absorptions. Thus, the cuvettes referred to earlier as "active" were those that did contain, in their construction, leachable lead glass. The "inactive" ones were apparently fabricated either without the use of lead glass or, if lead glass was used, the cuvettes were designed to avoid contact of the solder glass joints with the sample.

Indeed, substance has been added to this surmise when absorptions at 270, 302, and 357 nm were observed in spectra taken of halide solutions that had been in contact with fragments of lead-containing solder glass obtained from American Optical Company, Southbridge, Mass. A commercial product, Pyroceram Brand Cement (Corning Glass), in the form of finely divided glass designed for student use in the fabrication of glass apparatus, was treated in a similar way and again produced the characteristic absorptions at 270 and 301 nm.

Of course, the possibility that even the "pure" salts used in the earlier work may have been contaminated with lead cannot be ignored. In our laboratory, LiCl from a previously opened bottle produced a small absorption at 270 nm without contact with an "active" cell. Even after several recrystallizations, the peak (and, presumably, the lead contamination) was still present.

Due to the high extinction coefficients of the halo–lead complexes at their absorbing regions, very small concentrations of lead are detectable. It is possible to detect total Pb^{2+} concentrations of 10^{-6}M or less in concentrated halide solutions. This sensitivity may have analytical value in certain qualitative applications. We have been able to detect spectroscopically the presence of lead in the glaze of a certain brand of imported dinnerware which had been proclaimed by city health authorities as hazardous due to its lead content.

Direct Volatilization–Spectral Emission Type Detection System for Nanogram Amounts of Arsenic and Antimony

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An emission type detection system has been adapted for the detection and determination of arsenic and antimony. Arsenic and antimony compounds are converted to AsH$_3$ and SbH$_3$ in 1% aqueous NaBH$_4$. Arsine and stibine are swept out of the solution using He carrier gas, then passed through a CaSO$_4$ drying tube and through a dc discharge detector. The 228.8 nm As and 252.5 nm Sb emission line intensities are monitored in a conventional type photometric system. Limits of detection are near 0.5 and 1 nanogram for Sb and As, respectively. Operating conditions of the technique have been studied in detail. The method has been applied to the quantitative analysis of natural waters and some marine sludges. This method is highly specific, and is much more sensitive and rapid than most current methods for arsenic and antimony.

INTEREST IN THE DETECTION and determination of small amounts of arsenic and antimony compounds stems from their toxicity. Arsenic and antimony compounds have been widely used in insecticide products. A number of classical analytical methods have been developed for use in the field of forensic chemistry. The most widely used current methods for arsenic in low concentrations or small amounts are based upon colorimetric analysis after distillation of arsenic out of samples as arsine. The silver diethyldithiocarbamate method (*1*) for water analysis is an example. The lower limit of detection for this method is 0.2 μg As. Neutron activation methods have a limit of detection of 1 nanogram (*2*) but are comparatively time consuming and complex. Atomic absorption methods for arsenic have limits of detection in the range 0.5 to 1 ppm in the aspirated samples (*3, 4*). Using an electrodeless discharge lamp and an argon (entrained air) hydrogen flame, Menis and Rains (*5*) obtained detection limits near 0.1 ppm in the aspirated sample. Ando *et al.* (*6*) used a 91-cm path length and an argon (entrained air)–hydrogen flame to obtain a sensitivity (1% deflection) of 6 ppb.

Neutron activation (*2*) methods for antimony have limits of detection similar to those of arsenic. Atomic absorption methods for antimony (*7, 8*) have sensitivities (1% absorption) in the 0.3- to 1.5-ppm range. Rhodamine-B, a sensitive colorimetric reagent for antimony, is useful in the 2- to 20-μg range after extraction into benzene (*9*) or isopropyl ether.

(1) G. Stratton and H. C. Whitehead, *J. Amer. Water Works Ass.*, **54**, 861 (1962).

(2) V. P. Guinn and H. R. Lukens, Jr., data in "Trace Analysis: Physical Methods," G. H. Morrison, Ed., Interscience Publishers, New York, N.Y., 1965, p 345.
(3) W. Holak, ANAL. CHEM., **41**, 1712-13 (1969).
(4) G. F. Kirkbright and L. Ranson, *ibid.*, **43**, 1238 (1971).
(5) O. Menis and T. C. Rains, *ibid.*, **40**, 95 (1968).
(6) A. Ando, M. Suzuki, K. Fuwa, and B. L. Vallee, *ibid.*, **41**, 1974 (1969).
(7) S. Slavin and T. W. Sattur, *At. Absorption Newslett.*, **7** (5), 99 (1968).
(8) C. R. Walker, O. A. Vita, and R. W. Sparks, *Anal. Chim. Acta*, **47**, 1 (1969).
(9) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd ed., Interscience Publishers, New York, N.Y., 1959, p 254.