

NRL Report 6168

Fundamental Factors in Detecting Chemicals as Adsorbed Films

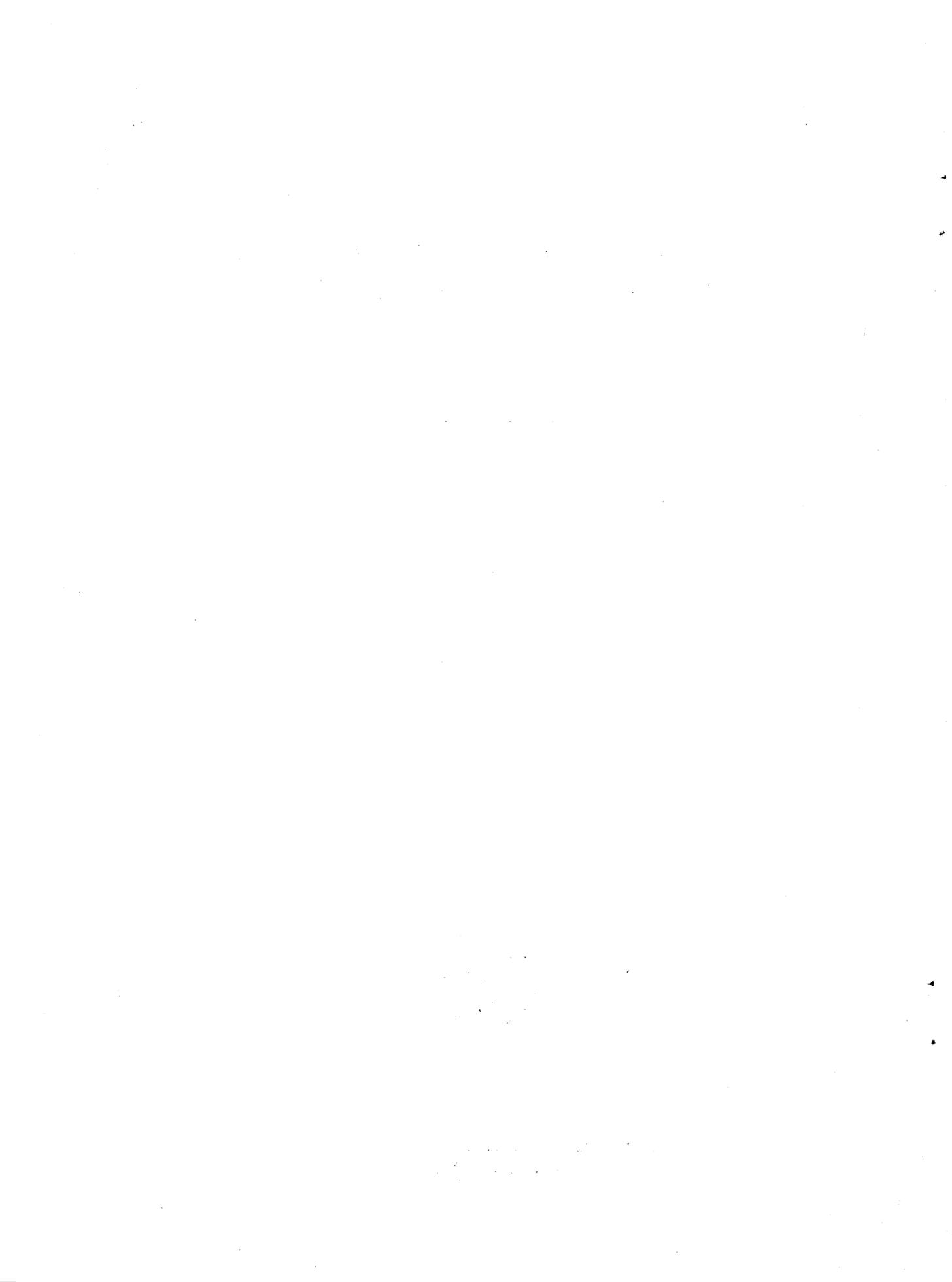
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ABSTRACT

Detection of trace chemicals in the atmosphere is possible by adsorption methods either through the results of physical adsorption or chemisorption processes. If the sensitivity of any such process is to be pushed to the limit, the ability to detect reliably the presence of a condensed monolayer or less becomes essential. Therefore, some of the general characteristics of surfaces and adsorbed monolayers deserve review with emphasis on the causes of the formation of the film and the conditions leading to optimizing the adsorption, the orientation, and the packing of the molecules to be detected. The nature of the forces responsible for adsorption will be reviewed briefly and related to the reversibility of the adsorption process and to the average lifetime of adsorption. Cooperative adsorption including surface micellization, or cluster formation, mixed films, and the helpful or limiting effects due to the presence of previously adsorbed materials will be discussed. Finally, some of the most sensitive methods of detecting and measuring the amount of adsorbed material will be reviewed with emphasis on their application to detection of chemicals in the atmosphere.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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FUNDAMENTAL FACTORS IN DETECTING CHEMICALS AS ADSORBED FILMS*

INTRODUCTION

For optimum sensitivity in detecting contaminants in the atmosphere the final recourse is: (a) to collect or accumulate the chemicals on some kind of adsorbing material, (b) to concentrate them, and (c) to detect and characterize them. Usually, some or all of these steps are made by utilizing surface properties. Therefore, the chemical and physical properties of material surfaces and adsorbed chemicals are fundamental to the subject of surface effects in detection. This report will first review certain basic physical chemical problems involved in detection of atmospheric contaminants and then will discuss available methods for optimizing the ability to collect, detect, and identify the materials present.

CLASSIFICATION OF SURFACES USED AS COLLECTORS

Obviously, the material surfaces used to collect the atmospheric contaminants may be either liquid or solid, and in turn each may be organic or inorganic. The solid surfaces may be crystalline or amorphous. The former may be ionic, molecular, or metallic crystal lattices. Another classification of solid surfaces would be in terms of the major differences in surface constitution, packing, and surface defects; however interesting that might be, such classification would be difficult to do at present.

A simpler and more useful method for classifying material surfaces is by the order of magnitude of the surface energy per unit area. With respect to liquid surfaces, the free surface energy per unit area is simply the surface tension (γ_{LV}) of the liquid-vapor interface. As is well known, at any given temperature there are large differences in the surface tensions of liquids. For example, metallic liquids having surface tensions of 200 to over 1000 dynes/cm are common, whereas the common inorganic liquids and all organic liquids at 20°C have surface tensions below 100 dynes/cm. Reliable data on (γ_0), the free surface energy per cm² of solids, are not available for most substances for two reasons. First, there are no direct experimental methods for measuring γ_0 , and no indirect method known applies to many kinds of solids. Second, the theoretical calculation of γ_0 is difficult and of doubtful validity because: (a) one must have a precise knowledge of the atomic structure of the solid, and (b) an important contribution originates in the outermost portion of the surface. However, both theoretical calculations as well as various extrapolations from the experimental surface tensions of the liquid phase through the melting point indicate that hard solids having high melting points, such as many common metals, inorganic oxides, and nitrides, have values of γ_0 ranging from about 500 to as high as 10,000 ergs/cm². A useful qualitative classification is to distinguish between hard, high-melting solids and soft, low-melting solids. The former class comprises solids having high specific surface energy, and the latter class comprises solids having low specific surface energy. In Table 1 is a useful comparison of these two extreme classes of solid materials.

An interesting distinction between solids of high surface energy and those of low surface energy is in their adsorbing, wetting, cohesive, and adhesive properties. Nearly all high-energy surfaces adsorb at ordinary temperature a great variety of compounds, and

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Table 1
Classification of Solid Surfaces by Surface Energy (γ_0)

High-Energy Surfaces	Low-Energy Surfaces
strong intermolecular forces	weak intermolecular forces
hard, high-melting, highly crystalline	soft, low-melting, poorly crystalline or amorphous
500 to 10,000 ergs/cm ²	less than 100 ergs/cm ²
inorganic (metals, oxides, nitrides, etc.)	organic (waxes, polymers, resins, etc.)

and the majority of liquids spread upon them spontaneously; low-energy surfaces adsorb a much smaller variety of substances, and very many liquids will not spread upon them spontaneously. On solids like the perfluorocarbons, which have the lowest surface energies known, few liquids will spread spontaneously, and their adsorptivity for most gases and vapor is very low unless cryogenic temperatures are used to create optimum conditions for polymolecular condensation following physical adsorption. In short, solids having low surface energy are physically more inert than those having high surface energy. Therefore, if one desires to find a surface capable of adsorbing efficiently a wide spectrum of compounds, a high-energy solid surface should be used; if a solid surface which resists adsorption is needed, a low-energy surface should be used.

INTERMOLECULAR FORCES

Excellent reviews concerning the forces between molecules or between molecules and material surfaces are available (1-4), and therefore it will suffice here to discuss briefly and approximately the essential features of the forces between molecules and atoms and the principal types of fields of force attracting molecules to solid or liquid surfaces. Let us consider the classic analytical expression for the potential energy of two well-separated clusters of electrical charges in the form of a power series of $1/r$, where r is the distance of separation between the two clusters:

$$V = \frac{1}{r} \sum_i e_i + \frac{1}{r^2} \sum_i e_i \ell_i \cos \theta_i + \frac{1}{r^3} \sum_i e_i \ell_i^2 \frac{3}{2} \left(\cos^2 \theta_i - \frac{1}{3} \right) + \dots \quad (1)$$

Here ℓ_i is the distance between the origin and the i th charge in the cluster. The first term on the right-hand side of Eq. (1) is the electrostatic or Coulomb potential energy arising from the net charge of each cluster. The second term is the electrostatic potential energy due to the interaction between the net dipole moment in each cluster. The third term is the electrostatic potential energy arising from interactions between the net quadripole moment of each cluster.

The number of terms needed for rapid convergence of this power series becomes greater as the two clusters come closer together, or as r becomes of the same order of magnitude as the largest dimension separating charges in either cluster. Obviously, the usefulness of this series expansion of V decreases as r becomes smaller and more series terms are needed for good convergences. However, when r is large enough, it is found that the potential energy (V), and therefore the force between clusters, can be considered as arising from superposition of the effects of (a) the Coulomb force between the net electrostatic charges, (b) the force between the dipoles, and (c) the force between quadripoles. Note that the dipole potential field varies as $1/r^2$ and the quadripole potential field as $1/r^3$.

When the clusters become nearer but do not penetrate, more terms are needed in the series expansion and Eq. (1) becomes more inaccurate as well as less tractable. Serious problems also arise through neglect of the quantum mechanical requirements for the allowable energy levels if there are electrons present in each cluster, since the cluster may be an ion, atom, or molecule. As London (5) first showed, the attraction between two like atoms having polarizability α and ionization potential I is given approximately by

$$V = \frac{3}{4} \frac{\alpha^2 I}{r^6} . \tag{2}$$

Especially important results of this and all subsequent studies of the London, or dispersion electron, field of force between electrically neutral atoms or molecules are that (a) when $r > r_e$ the field is always attractive and (b) as r decreases, the intensity only becomes appreciable at distances of a few atom diameters. Figures 1A and 1B illustrate these points through plots of the potential energy (V) and the field intensity (F) as functions of r . Much effort has been spent in wave mechanical calculations of the field between various simple atoms or molecules; however, theoretical calculations become very difficult for more complex atoms and molecules. An example is given in Fig. 2 of a plot by Hirschfelder et al. (2) of the calculated and experimental data on V as a function of r for the force field between two argon atoms.

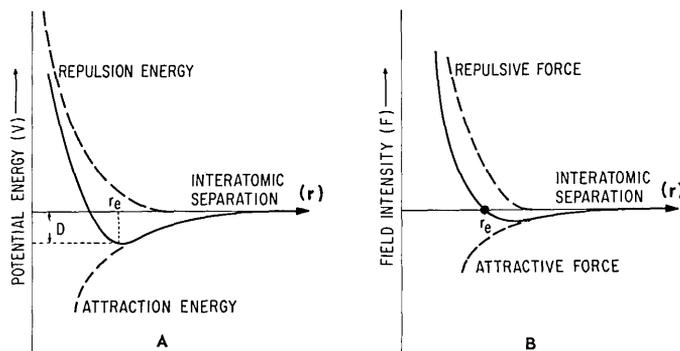
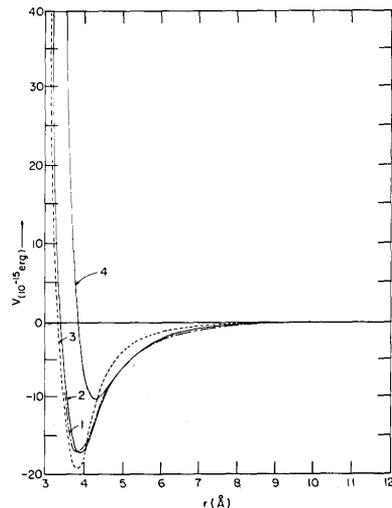


Fig. 1 - Typical interatomic fields (here r_e is the equilibrium distance between atoms)

Fig. 2 - Four potential curves for the interaction between two argon atoms. (1) An experimental curve of the Lennard-Jones form from viscosity. (2) An experimental curve of the modified Buckingham form fitted to the data on the second virial coefficient and properties of the crystal (Mason and W.E. Rice). (3) An experimental curve due to O.K. Rice. (4) The theoretical results of Kunitzune, modified to include the dispersion energy. These data are from Ref. (2).



When the clusters of charges are in contact, exchanges of the charged particles can occur; if the clusters are atoms, such exchanges, especially those of the orbital electrons, gave rise to resonance, ionization, or to the formation of the various types of chemical bonds. But here the extent of cluster interpenetration is restricted because strong electrostatic repulsions develop between nuclei, and hence the atoms and molecules act as if they have a definite shape and size.

Important features of the intermolecular forces are summarized in Tables 2 and 3, which are due to London (5) and Stuart (6), respectively. Table 2 shows that the London attraction is the overwhelming contributor to the potential energy between two atoms or molecules which are not in contact and do not have unusually large polarizabilities. For example, in the case of two molecules of carbon monoxide, the energy of the London field is 67.5 units, whereas that arising from the permanent and induced electrostatic dipole moments is only 0.0034 and 0.057 units, respectively. The only exceptions are substances like water and ammonia with large dipole moments and modest polarizabilities.

Table 3 shows that the energy arising from the London dispersion electron attraction is a very significant contribution to the potential energy when the molecules are separated about 3 Å. The energy arising from the interaction of permanent dipoles with permanent or with induced dipoles is more significant than the London field contribution when the distance of separation is about 10 Å. At separations of 100 Å or more the London and the dipole-dipole fields are insignificant. Finally, the range of electrostatic interaction between an ion and a dipole is much less than that of an ion with an ion when they are separated 100 Å or more.

This survey emphasizes that the forces between any two atoms or molecules (other than large polymers) will be insignificant at distances over about 10 Å unless the atom or molecule is ionized.

Adsorption forces between a molecule, a colloidal particle, or a solid, and another solid (or liquid) surface are difficult to measure or compute. In the first case, the experiments require observations of exceedingly small forces between particle and surface unless their separation becomes of the order of 10,000 Å or less. At such separations the experimental problems with surface roughness, vibration, and electrostatic charge effects become grave. Calculations by integration of the forces between the individual atoms and molecules of the particle and surface are difficult because a precisely ordered and uniform solid or liquid is required for success, and the interaction of the atoms with the materials must be taken into careful account in terms of the order in the structure. Few experiments reported have been entirely convincing; the most impressive has been the investigation of Derjaguin and Abrikossova (7). Even that has been considered sound by many investigators mainly because the measurements agreed with calculations. These were based on the theoretical work of Lifshitz et al. (8) in which the materials were considered as continuous media. Calculations of the attractive force between two plane solids have been made for metals and also for nonmetals. Results on the latter predict the force will vary as the inverse fourth power of the distance separating them; estimates have been made that there will be a perceptible attraction at separations of 1000 to 10,000 Å.

It is pertinent that in our own studies of the adhesion of liquids on solid surfaces (9), we found that coating the solid surface with a uniform and condensed monolayer of an 18-carbon fatty acid, primary amine, or alcohol only one molecule thick (approximately 24 Å) completely changed the wetting and the liquid adhesive properties. Furthermore, a solid surface coated with such a film had the same wetting properties regardless of the nature of the solid beneath. Thus, whether or not the monolayer rested on borosilicate glass, quartz, platinum, gold, nickel, or chromium, the coated surface behaved the same. Such observations are good evidence that the attractive forces of the supporting metallic or nonmetallic solid cannot be significant at a distance of 24 Å from its surface.

Table 2
Contributions to Intermolecular Energy Between Like Polar Molecules*

Molecule	Ionization Energy (electron volts)	Polarizability (10^{-24})	μ Dipole Moment (10^{-18} esu)	Intermolecular Potential Energy $\times 10^6$		
				London Dispersion (10^{-60} erg-cm ⁶)	Induced Dipole (10^{-60} erg-cm ⁶)	Permanent Dipole (10^{-60} erg-cm ⁶)
CO	14.3	1.99	0.12	67.5	0.057	0.0034
HI	12.0	5.4	0.38	382.0	1.68	0.35
HBr	13.3	3.58	0.78	176.0	4.05	6.2
HCl	13.7	2.63	1.03	105.0	5.4	18.6
NH ₃	16.0	2.21	1.5	93.0	10.0	84.0
H ₂ O	18.0	1.48	1.84	47.0	10.0	190.0

*From Ref. 5 calculations for T = 293 Kelvin.

Table 3
Contributions to Intermolecular Field Energy of Two Molecules at Various Separations*

Nature of Interaction	Energy Relation	Intermolecular Energy at Following Values of r :			Effective Range of Field (Å)
		3Å	10Å	100Å	
Dispersion Electron	$\frac{3}{4} \frac{a^2 I}{r^6}$	1.5×10^{-13}	0.1×10^{-15}	Negligible	4.0
Dipole-Dipole	$\frac{2\mu^2}{r^3}$	1.6×10^{-13}	5.0×10^{-15}	0.05×10^{-16}	5.0
Ion-Dipole	$\frac{e\mu}{r^2}$	8.5×10^{-13}	77.0×10^{-15}	7.7×10^{-16}	14.0
Ion-Ion	$\frac{e^2}{r}$	80.0×10^{-13}	2500.0×10^{-15}	2500.0×10^{-16}	500.0

*From Ref. 6, assuming $a = 2.5 \times 10^{-24}$, $\frac{3}{4} I = 100 \times 10^{-60}$ erg cm⁶, and $\mu = 1.6 \times 10^{-18}$ esu.

THE BASIC ROLE OF PHYSICAL ADSORPTION IN COLLECTION OF CONTAMINANTS

Physical adsorption methods are widely used to collect or accumulate the atmospheric contaminant chemicals on material surfaces. Therefore, the advantages and limitations of nearly all collecting methods are determined by certain characteristics of physical adsorption. First, physical adsorption of a compound on a solid or liquid surface takes place without the formation of a chemical compound or chemical bond with atoms in the surface phase. Second, physical adsorption of any molecule not occupying more than one adsorption site is always an exothermal process, the heat evolved rarely exceeding 10 to 15 kcal/mole. Since the average kinetic energy of the molecules per degree of freedom at equilibrium is $(1/2) kT$, and since the adsorbed molecules have only two degrees of freedom, the average molecular kinetic energy for mobile adsorption is kT . When kT exceeds q , the heat of adsorption per molecule, the desorption process becomes dominant, and one can estimate roughly the upper limit of the temperature for physical adsorption of the given compound and surface by the relation

$$kT = q. \quad (3)$$

Hence, physical adsorption is reversible with temperature and pressure. Obviously, it is a great advantage in collection to keep the adsorbing surface at as low a temperature as possible.

Hydrogen bonding between the adsorbed molecules and those constituting the surface phase plays an important role in physical adsorption. Usually when q is more than a few kcal/mole, but less than 15, hydrogen bonding is involved. Thus the primary amines, the carboxylic acids, alcohols, and phenols, adsorb strongly on surfaces containing atoms which readily donate or accept hydrogen bonds; examples are the acidic and basic surfaces, oxidized metals, crystalline solids containing water of crystallization, and surfaces covered in whole or part with adsorbed water.

Molecules having a permanent dipole moment (μ) will always be attracted to that surface because of the electrostatic "image" effect of the charges induced in its surface. Hence, if the metal surface can be treated as an ideal, continuous, plane conductor, the energy of adsorption of the molecule is given by

$$U = \frac{\mu^2(1 + \cos^2\theta)}{8d^3}. \quad (4)$$

Here θ is the angle between the dipole axis and the normal to the surface and d is the distance to the adsorbing surface from the electrostatic center of gravity of the molecular dipole. This relation was first discussed in relation to the heat of adsorption by Lorenz and Landé (10). Later research has recognized that Eq. (4) can be correct only when d is much larger than a few atom diameters. When d is smaller, the discontinuous nature of the metal and the phase relations of electrons in the adsorbed molecule and solid surface cannot be neglected. It is recognized that the correct relation should involve parameters characteristic of the metal surface, as well as the polarizability α of the adsorbed molecule, but that U would vary as $1/d^3$. It can be concluded that the electrostatic image force contribution (4) to the adsorption energy of the molecule to a solid surface is usually small in comparison to that resulting from the rapidly fluctuating interactions between the electrons in the adsorbed molecule with the electrons in the solid surface.

Since the dispersion electron field between molecules is always attractive, one would expect that polar or nonpolar molecules will always be attracted to any solid or liquid surface by the dispersion forces between it and the atoms, ions, and electrons in the surface of the solid. deBoer (11) has repeatedly argued that atoms and molecules must

Table 4
Contact Potential Differences of Metals Due to
Physically Adsorbed Films†

Metal	Gas	Contact Potential Difference (volts)	Metal	Gas	Contact Potential Difference (volts)
Ti	Xe	+0.84	Hg	C ₂ H ₄	+0.27
Cr	Xe	+0.95	Hg	C ₂ H ₂	+0.21
Fe	Xe	+0.66	Ni	C ₂ H ₆	+0.77
Ni	Xe	+0.85	Ni	C ₂ H ₄	+0.83
Cu	Xe	+0.66	Ni	C ₆ H ₆	+1.3
Zn	Xe	+0.21	W	Xe	+1.1
Hg	Xe	+0.23	Cu	N ₂	+0.45*
Hg	O ₂	+0.03*	Cu	CH ₄	+0.14*
Hg	CH ₄	+0.16*	Cu	C ₂ H ₆	+0.69
Hg	C ₂ H ₆	+0.23	Cu	C ₂ H ₄	+1.23

†Reference 12.

*Incomplete coverage.

always be polarized when adsorbed on the surface of any solid, especially on the surface of an ionic crystal or a metal. Mignolet (12) strengthened this conclusion by his contact potential experiments in high vacuum on the effect of adsorbing xenon, nitrogen, or methane on various metal surfaces. Table 4 summarizes his results on the contact potential difference between a gold reference electrode and the metal (listed in the first column) resulting from the adsorption at subzero temperatures of various nonpolar gases. For example, xenon, which has no dipole moment in the gaseous state, upon adsorbing on nickel caused the large contact potential change of 0.66 volt. This result can only mean that each xenon atom is polarized by induction while adsorbed on the surface of nickel. Our recent investigation (13) of the polarization of nonpolar liquid molecules adsorbed on numerous metals has shown that much more complex organic molecules like hexane, octane, decane, hexadecane, carbon tetrachloride, benzene, and toluene, also have large electrostatic moments induced by physical adsorption, and the effects are readily detected in films adsorbed on metals in the air. Hence, both theory and experiment agree that all atoms and molecules become polarized by induction through adsorption upon metals; very probably a similar process occurs on any solid or liquid surface.

For these reasons it is necessary in concentrating unionized molecular contaminants from the atmosphere to flow the contaminated gas over as large an area of solid or liquid surface as possible and to use conditions of flow which maximize the probability that the contaminant molecules will either impinge on the surface or come close enough to be attracted by the forces emanating from the material surface.

Let us consider a few general concepts basic to the kinetic theory of gaseous adsorption which originated with Langmuir (14) and have been fully discussed by deBoer (15). If the rate molecules impinge on a unit area of solid surface is m , and if ν is the rate of evaporation of the adsorbed molecules from unit area of surface, the rate of adsorption per unit area will be

$$\frac{ds}{dt} = am - \nu \quad (5)$$

where s is the surface concentration of adsorbed molecules and a is the condensation coefficient (or ratio of the number of molecules condensing per unit time to the total number striking that surface). At adsorption equilibrium,

$$\frac{ds}{dt} = 0$$

and therefore

$$am = \nu . \quad (6)$$

The simple and general equilibrium relations given in Eqs. (6), (7), and (8) are valuable in discussing physical adsorption. Langmuir (14) discussed early how m depends on the molecular weight, temperature, and vapor pressure of the adsorbing molecule. Frenkel (16) soon afterwards stated how ν depends on q , the energy of adsorption per molecule. Only those molecules will desorb whose kinetic energy is greater than q ; hence, the rate of evaporation ν is given by

$$\nu = k_0 e^{-q/kT} \quad (7)$$

The ratio ν/s is the average probability per second for the evaporation of the molecules. The average lifetime (τ) of the adsorbed molecules on the surface will be given by

$$\tau = s/\nu = \frac{s}{k_0} e^{q/kT} . \quad (8)$$

In collecting chemicals from the atmosphere by physical adsorption, it is obvious that m should be as large as possible; however, m is a property of the gas contaminant to be adsorbed, and so it is not controllable. A major problem in designing the collector is to make s , and hence τ , as large as possible. Equation (8) shows that to do so it is essential to make ν as small as possible; from Eq. (7) this is equivalent to requiring that q be as large and the temperature T as low as possible. In other words, for maximum collection by adsorption for a given rate of impingement of molecules on the surface, it is necessary to employ a material surface having the optimum heat of adsorption for such molecules and to chill the collecting surface as much as possible. Making q large is a major problem in selecting suitable adsorbing materials. Usually, a high-energy surface is required. Obviously, other problems are: (a) to increase the area of contact of the gas phase with the collecting surface, and (b) to circulate the atmosphere over the surface in such a way as to increase the probability of molecular impingement.

A major problem in employing physical adsorption methods to detect atmospheric contaminants is that of identifying or characterizing the material collected and concentrated on the adsorbing surface. All compounds physically adsorb to some extent on any material surface, and the differences in adsorptivity of the chemicals in most mixtures are not sufficient to characterize them readily.

PROBLEMS OF CONCENTRATING CONTAMINANTS

If the partial pressure (p) of a contaminant in the atmosphere is much below the saturation pressure (p_0), as is usually the case, the adsorbed film will not be polymolecular. Indeed, the surface coverage by the adsorbed monolayer will also be low, and the problem of accumulating sufficient contaminant on the adsorbing surface to permit reliable detection becomes dominant. Obviously, a means of concentrating the collected material would be helpful.

Various concentrating techniques and devices have been used. For example, the contaminant after being collected in a gas-liquid partition chromatographic column, which may be chilled, is removed in a more concentrated form by heating or by displacement with a more adsorptive gas or volatile solvent. A more recent method takes advantage of the fact that the retention volume - the volume of carrier gas required to move a substance completely through the chromatographic column - varies exponentially with the reciprocal of the temperature. It is therefore possible to pass a large volume of contaminated air through a capillary adsorption column made by wetting the interior of a coiled copper tube with the appropriate liquid. At some low temperature the tube will completely retain all the contaminants in the column whose retention volumes are greater than the volume of the sample. Subsequent heating of the column and backflushing it with a suitable carrier gas will release the contaminants into a much smaller volume of gas than the original sample. Hence, a large increase can result in the gaseous concentration of the trace contaminants. This method has been employed at NRL by Umstead (17) using the copper coil chilled at 0°C to obtain a thirtyfold increase in the concentration of trace hydrocarbon contaminants in the atmosphere of a submerged nuclear submarine.

Large concentrating effects can be obtained by bubbling the contaminated atmosphere into an appropriate solvent of low volatility until sufficient material has accumulated in solution. Then the solution can be treated by bubbling through it a carrier gas, like helium, which will displace the solute and carry it into a liquid gas partition chromatograph to be fractionated before delivery to a detector. The efficiency of displacing the solute can be greatly increased and expedited by use of a miniature on-stream gas stripper such as that recently described by Williams and Miller (18) which will work efficiently with a few ml liquid samples and require only a few minutes. Of course, such an approach depends for its efficiency on the values of the gas-liquid partition coefficients of the contaminants.

COLLECTION AND/OR DETECTION THROUGH CHEMISORPTION

Chemisorption is defined as the reaction of the chemical adsorbed with the surface atoms of the solid to form a compound; hence, some kind of chemical bond is formed. As Langmuir first pointed out (14) chemisorption never exceeds a monolayer. Chemisorption is not reversible with pressure, nor with ordinary changes in temperature, because the energy of the reaction with the surface is usually much larger than kT . Another feature of chemisorption is that it is highly specific; hence the process can be used to select (or identify) one type of compound from a variety of chemicals in the atmosphere. However, there results the problem of regenerating the adsorbing surface to permit its repeated use in detection. This is not a difficulty in applications like those made of detector tubes for specific gases, because they are inexpensive enough to be used only once; well-known examples are the Dräger (19) and Mine Safety (20) detector kits for atmospheric contaminants. A recent example due to Williams and Miller (21) is the use of a reagent adsorbed on silica gel and packed into a small open-ended glass tube to detect 1 part per 10^6 by volume of ammonia or monoethanolamine. The atmosphere is hand pumped through the tube for a definite time while the adsorbed reagent reacts to exhibit a characteristic blue color.

SENSITIVE METHODS OF DETECTION

Although there are innumerable methods of detecting and identifying specific kinds of contaminants in the atmosphere, many are not sufficiently sensitive, others are too time consuming, and none are suitable for all problems. It is a remarkable fact that no present method of detection is more sensitive and reliable than is the normal human nose with respect to certain chemicals. Table 5 gives a tabulation (22) on the threshold concentration for detection by odor. As little as one part in 10^{13} of vanillin and skatol, and four

Table 5
Odor Thresholds for Common Odorous Materials*

Substance	Threshold Concentration (ppm)
Vanillin	1.7×10^{-7}
Skatol	3.3×10^{-7}
Synthetic musk	4.2×10^{-6}
Mercaptan	3.3×10^{-5}
Butyric acid	8.3×10^{-4}
Chlorophenol	3.3×10^{-3}
Iodoform	5.0×10^{-3}
Natural musk	5.6×10^{-3}
Pyridine	3.3×10^{-2}
Diethyl ether	8.3×10^{-1}
Phenol	1
Sulfur dioxide	3.0
Chlorine	3.5
Ammonia	5.3×10

*From Ref. 22.

parts in 10^{12} of musk, eight parts in 10^{10} of butyric acid, eight parts in 10^7 of ethyl ether, and five parts in 10^5 of ammonia can be detected. However, the sense of smell is qualitative and varies greatly among people and animals. Many common contaminants of importance do not have an odor, and when in mixtures many chemicals cannot be distinguished.

Ozone in the atmosphere can be detected in a portable device in concentrations of only five parts per 10^9 (23,24). The contaminated atmosphere is bubbled into a buffered aqueous solution of potassium iodide, the iodine liberated is adsorbed and depolarizes the platinum electrodes of an amperometer. The concentration of O_3 is measured by amount of sodium thiosulphate required to return the electric current to its original value. This method, which is a modification of that described by Gluckauf et al. (25), is an example of a sensitive method which depends upon detecting the contaminant after it has adsorbed on a solid surface. It also has the ability to develop increased sensitivity by accumulating (or concentrating) the contaminant in a solvent.

The equilibrium contact angle exhibited by water (and many other liquids) on a polished solid surface on which the atmospheric contaminant had adsorbed is a test which is especially sensitive to organic contaminants (8). It has long been known that the presence of many kinds of organic contamination on a solid surface is readily detected by the large hydrophobic contact angle; this is the basis for the "water break" test (26). Surface-chemical research has shown that it is easy to detect hydrocarbons, as well as many other organic contaminants, when enough molecules have accumulated on the surface to the extent of only 10% of a close-packed adsorbed monolayer (9). Despite its sensitivity, this method is not specific enough to allow identification of many contaminants.

Ellipsometry, or the detection of a film on a solid surface by the elliptical polarization of a reflected beam of plane polarized incident light, is a well-known method for studying adsorbed films (27-29). This method has certain limitations, one of which is that the

adsorbing surface must be a mirror plane to within a quarter wavelength of light. Also, the material used must have high reflectivity; therefore, for extreme sensitivity, the surface must be of silver, chromium, nickel, or platinum. A film as thin as an adsorbed monolayer of a fatty acid can be detected with an ellipsometer with a precision of ± 5 to 10%. However, analysis of the desired data requires accurate knowledge of the refractive index of the adsorbed film. Only in special cases could identification be made by this method. At present ellipsometry is more valuable as a research tool in a special laboratory than for recognizing or identifying the adsorbed monolayers characteristically encountered in the most sensitive systems for detecting contamination; therefore, it is not as promising as some of the other methods in the field of surface effects in detection.

The contact potential difference between two metals is extremely sensitive to the presence of any adsorbed film on either metal (30,31). Under ideal conditions, as little as a few percent of a close-packed monomolecular film can be detected. This method has been difficult to employ in the past not only because water adsorption causes a major effect but also because adsorption of contaminants from the atmosphere occurs on both metal surfaces; hence, the contact potential difference observed is the net result of two different adsorption processes which under some circumstances can cause effects of opposite polarity. These difficulties have become less prominent in the past decade through control of temperature and relative humidity as well as the introduction of special coatings on one electrode to make it less active in adsorbing contaminants from the atmosphere and so able to operate as a "reference" electrode (32,33) suitable for work with some vapors. Especially useful is a reference electrode made of gold or platinum coated with a film of Teflon or FEP Teflon. The vibrating condenser method of measurement (34) or the automatic recording system based on a modified ionization method due to Bewig (35) appear to be capable of much future service in the detection of atmospheric contamination. There is at present only a meager amount of reliable data in the literature on the effects on the contact potentials of adsorbing various chemicals. This particular aspect of the subject has been reviewed in other reports (33,36).

An adsorbed film of organic material has a remarkable damping effect on a capillary wave or ripple on the surface of a liquid such as water or mercury. Garrett and Bultman (37,38) have shown only recently that essentially all of this wave damping effect has been accomplished when an organic monolayer has adsorbed on the surface and created a film pressure (or surface tension lowering) of only 1 dyne/cm; this means that the total damping effect is caused by a monolayer which is not even close packed! In principle, the effect of organic contaminants on wave damping could be used as a sensitive detector. However, it is only possible in the absence of extraneous vibrations and not likely to be a useful method for the near future; certainly, it does not look promising for a portable method.

Thermal conductivity bridges have been much used in the past decade as detectors in gas-liquid chromatographic systems. Four small heated resistors, which may be transistors, each forming a thermal conductivity or Pirani cell, are mounted in a block of metal but insulated electrically and are connected into a Wheatstone bridge arrangement, and the bridge is balanced electrically with the usual amplifier and detector. Any change in the nature of the gas flowing past two of the four heated resistance wires of the bridge will affect the rate of heat transfer and therefore upset the balance of the bridge. The sensitivity of the thermal conductivity bridge to any contaminant obviously will increase with the difference between the conductivity of contaminant and air. Minter (39) has developed a portable bridge for detecting the leakage of gases from a pressurized system provided that the thermal conductivity of the leaking gas is different from that of air, and a smaller transistorized version of this detector, subsequently developed by Hafner (40), is now being used by the U.S. Navy to detect small Freon leaks in the air-conditioning system of nuclear submarines. The same device is a very sensitive leakage detector for many other gases.

Mass spectrometry as well as infrared spectrophotometry are now being used for identifying contaminants in the atmosphere. However, the problem of obtaining high sensitivity can be very great unless the specimens are first concentrated as much as possible.

Fortunately, many sensitive physical methods such as contact potential measurements, thermal conductivity bridges, infrared spectrophotometers, mass spectrometers, and gas ionization methods are readily adapted to use with a gas-liquid partition chromatograph (41,42). The atmospheric sample injected is separated by the column into various fractions made up of molecules having the same retention time, and each is successively delivered directly to the associated detecting device. Subsequently, a fraction may be condensed and delivered via a microsyringe to some specific detector for identification of the individual compounds. The fraction collector invented by Saunders (43) is particularly effective, if the latter route is chosen. At present the limitations in the use of these valuable devices for concentrating and analyzing contaminants are: (a) the lack of portability of the more refined types of equipment and (b) the fact that highly trained operators are needed to interpret reliably the instrument recordings. The chromatograph in one form or other offers the most effective and widely applicable devices for collecting, concentrating, and analyzing contaminants in the atmosphere. Undoubtedly, they will become increasingly more versatile and portable.

An example of what is being done today with gas-liquid partition chromatography techniques when combined with infrared absorption spectrometry is given in Table 6 which summarizes some of the analytical results obtained by Kagarise and Saunders (44) on the trace constituents in aviators' breathing oxygen. This problem arose because it was believed that traces of impurities in the compressed oxygen were the cause of nausea experienced by some aviators after breathing it over an extended time. Attention is called to the many trace contaminants present in the allegedly pure oxygen in concentrations of parts per million or less.

Table 6
Contaminants in Aviators' Breathing Oxygen*

Contaminant	Formula	Concentration (ppm)	
		Cylinder #16	Cylinder #17
Carbon dioxide	CO ₂	3.1	3.4
Nitrous oxide	N ₂ O	0.30	0.31
Acetylene	C ₂ H ₂	0.20	0.15
Ethylene	C ₂ H ₄	0.05	0.033
Propane	C ₃ H ₈	trace	0.056
iso-Butane	C ₄ H ₁₀	0.012	0.012
n-Butane	C ₄ H ₁₀	0.038	0.044
iso-Pentane	C ₅ H ₁₂	0.025	0.012
n-Pentane	C ₅ H ₁₂	0.015	0.036
C ₆ -hydrocarbons	C ₆ H ₁₄	Trace of three compounds	Trace of six compounds

*From Ref. 44.

CONCLUSIONS

Certainly the three most difficult, important, and unsolved problems in detecting contaminants in the atmosphere are: (a) finding a method which is sufficiently general, i.e., applicable to whatever the contamination may be, (b) finding a sensitive device which also is portable and reliable enough for field activities, and (c) detecting biological contamination, such as undesirable bacteria, in the atmosphere without requiring long delays for the development of cultures before reliable identification. Many of the most sensitive detecting devices known are only effective for specific contaminants. Some devices lose their effectiveness once the contaminant has accumulated on the receptor surface; in other words, in many instances the early contaminants adsorbed desensitize the detector surface and either decrease its sensitivity or prevent it from being used at all. The problem of portability and reliability in detecting and identifying contaminants has not yet been adequately solved even for specialized forms of detection such as in chemical or biological warfare, unless one considers the limiting case where the detection is only confined to one or several specific contaminants. New and more sensitive detecting devices are needed. Probably the new detectors, like those now available, will have to be used along with some device which separates as many as possible of the contaminants into distinct groups or individual compounds before presenting each separately to the detector. At present, some form of chromatographic adsorption or partitioning column is the most promising device.

In conclusion, it may be a mistake today to concentrate too large a proportion of the effort on finding more sensitive detectors of contaminants in the atmosphere. What is usually needed is a complete system of which the detector is only one part. Much also can be done to take some of the burden off the detector by designing the entire system for accumulating the contaminants from the air and (if possible) concentrating them before delivering the resulting material to the detecting or characterizing device.

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13. ABSTRACT Detection of trace chemicals in the atmosphere is possible by adsorption methods either through the results of physical adsorption or chemisorption processes. If the sensitivity of any such process is to be pushed to the limit, the ability to detect reliably the presence of a condensed monolayer or less becomes essential. Therefore, some of the general characteristics of surfaces and adsorbed monolayers deserve review with emphasis on the causes of the formation of the film and the conditions leading to optimizing the adsorption, the orientation, and the packing of the molecules to be detected. The nature of the forces responsible for adsorption will be reviewed briefly and related to the reversibility of the adsorption process and to the average lifetime of adsorption. Cooperative adsorption including surface micellization, or cluster formation, mixed films, and the helpful or limiting effects due to the presence of previously adsorbed materials will be discussed. Finally, some of the most sensitive methods of detecting and measuring the amount of adsorbed material will be reviewed with emphasis on their application to detection of chemicals in the atmosphere.		

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