Lead concentration in city air increases

WATER, AIR & WASTE

Like many other air pollution issues, the facts about leaded gasoline and its impact on air and public health have been little known and are often contradictory when they are known. Some light was shed on an otherwise cloudy subject, however, when Dr. Tsaihwa J. Chow told participants that he, John L. Earl, Carrie Snyder, and coworkers at Scripps Institution of Oceanography and University of California San Diego, La Jolla, Calif., have isotopically identified leaded gasoline as the overwhelming contributor of lead pollutants to the atmosphere.

This conclusion stems from Dr. Chow's three-year study of lead concentrations in the San Diego, Calif., area sponsored by the U.S. Public Health Service. Other conclusions:

- In the San Diego region, the atmospheric lead concentrations show an annual cycle, with a winter high and a summer low.
- A long-term increasing trend of lead content in the air is observed as compared with 1957 and 1965 data.
- Geographically there is a logarithmic increase of atmospheric lead content from midocean to remote high mountains and from seashore to suburban and urban locations.
- During the temperature inversion phenomenon, lead content of downtown San Diego air approaches 8 micrograms per cubic meter of air, nearly that of the tentative national air quality limit.
- Lead aerosols constitute as much as 7% of total suspended particulate material in the air.
- Midpacific marine air with lead concentration of 0.001 micrograms per cubic meter is the least polluted of northern temperate atmospheres.

Sampling. Dr. Chow's team has collected air samples at four stations representing various environmental conditions in the San Diego area. The Mount Laguna station, elevation 6100 feet, located at the Astronomical Observatory on the crest of the peninsular range, is remote from any industrial sources of pollution. The San Diego metropolitan area is about 45 miles west of this site. Automotive traffic within a half mile of the station is less than a dozen cars per week. Lead concentration at this location, Dr. Chow finds, is uniformly low throughout the year with an average of 0.05 micrograms per cubic meter.

> Lead was introduced into gasoline to raise its octane rating 47 years ago. Each gallon of today's gasoline has about 4 grams of lead in it, which adds up to 700 million pounds of lead consumed each year by gasoline sales. While there is not hard agreement about how much lead gets exhausted into the air, most experts say that about 70% of the lead in gasoline comes out of a car's tailpipe. A conservative estimate is that half the exhausted lead gets airborne, meaning that at least 250 million pounds of lead swirl into the air every year from automobile exhausts.

Scripps Institution's sampling site is located at the end of an observation pier which extends 1000 feet into the Pacific Ocean. This site shows relatively low lead content, about 0.4 micrograms per cubic meter, especially during summer months.

The Mission Valley station is about 10 miles inland from the ocean in a broad flat-floored valley transecting the heavily populated San Diego mesa. The valley floor is being increasingly developed with major shopping centers, hotels, and sports facilities. Several major freeways and highways either follow the valley or transect it. Traffic flow in the vicinity of the station is about 175,000 cars per day. Not surprisingly, lead content in this area has been increasing over the years of the study, with a 1969 mean of more than 2 micrograms per cubic meter.

The downtown San Diego station is in a commercial area; however, traffic flow downtown has not increased as fast as in most other parts of the city. Dr. Chow concludes, based on three years of sampling in this area and on some earlier work by Bureau of Air Sanitation and National Air Sampling Network, that lead concentration appears to increasing at a rate of about 5% a year.

Filters. Sampling operations involve continuous pumping of air through filters for periods of seven days. Air sampling gear consists of vacuum pumps which draw air through MF-Millipore cellulose ester membranes, type HAWP, with a 0.45-micron mean pore size and a retention efficiency of more than 95% for 0.05-micron particles.

The filter holder is made of anodized aluminum with a gold plated screen and a clamp ring to support the filter. Filter holders are housed in inverted polyethylene cups for protection from rain, dust fall, and sea spray and are suspended from wooden poles extending from the roof of the building.

Dr. Chow's group dissolves the exposed filters in concentrated nitric and perchloric acids, spiked with lead-206 tracer. The team isolates lead by standard ion exchange techniques, purifies it by several dithizone extractions, and then converts it to a sulfide. It then analyzes the samples by mass spectrometry to determine lead isotope ratios. This technique is known as isotopic dilution.

From thousands of air samples collected over more than three years the California group is able to determine seasonal trends of weekly lead concentrations at San Diego, Mission Valley, and Scripps Institution. It finds that atmospheric lead concentrations show an annual cycle with a winter high, summer low. Dr. Chow attributes this pattern of seasonal variation to local meterological conditions.

Summer months, explains Dr. Chow, in southern California are usually

John Earl (left) and Dr. Chow analyze lead aerosols by mass spectrometry

Dr. Story (left) and Dr. Busch analyze products of peroxide fragmentation

fraction of the cost of present methods, Dr. Story says.

Mixed peroxides. The most important new development since Dr. Story's original 1968 publication of his procedure is his discovery of methods of generating mixed trimeric peroxides in good yield. The decomposition of symmetrical dimeric and trimeric peroxides was previously accomplished by the Georgia scientist. But to make the method truly general and extend it to synthesis of all size rings, substituted and unsubstituted, it is necessary to synthesize unsymmetrical peroxides.

The key intermediate in the synthesis of mixed trimeric peroxides is 1,1'-dihydroperoxydicyclohexyl peroxide, prepared by a new method giving quantitative yields. In a typical reaction, this dihydroperoxide is stirred with cyclopentanone and anhydrous cupric sulfate at room temperature for 13 days. Addition of a large excess of water and recrystallization of the crude product from methanol give a 58% yield of the 6-6-5 trimeric peroxide.

Decomposition of the mixed 6-6-5 trimer by refluxing in decane yields cyclotetradecane and 15-pentadecanolide, in 17 and 22% yields, respectively. These rings are not otherwise available, except through cyclooctanone diperoxide—which is obtainable only in low yield.

Many mixed tricycloalkylidene peroxides have been synthesized and converted to the corresponding macrocyclic compounds. The 12-12-7 trimeric peroxide gives a C_{28} hydrocarbon ring and a C_{29} lactone on thermal decomposition, in 30% and 10 to 15% yields, respectively. Some of the macrocyclic compounds obtainable from the mixed peroxides cannot be synthesized from any readily available symmetrical peroxide.

The utility of the method depends considerably on the availability of the dihydroperoxide. Dr. Story and Dr. Busch have recently developed a new procedure for preparing it in very high yield. Typically, it is synthesized by stirring for five hours, at room temperature in an open crystallization dish, a mixture of 90% hydrogen peroxide and cyclohexanone in 2:1 molar proportions, together with several drops of 70% perchloric acid catalyst in acetonitrile. The mixture becomes a crystalline mass, is washed with water, and recrystallized from hexane, giving a quantitative yield of 94% pure dihydroperoxide. Besides the 6-6 dihydroperoxide, Dr. Story has also prepared 5-5, 7-7, 8-8, 12-12, and other peroxides in good yield.

Substituted macrocyclics. Perhaps even more important than other applications, monosubstituted macrocyclic compounds can be synthesized by the ketone peroxide fragmentation method. For example, methoxycyclopentadecane can be prepared in 35% yield, by reacting 1,1'-dihydroperoxydicyclohexyl peroxide with 4-methoxycyclohexanone for two to three hours at −10° C. in propionic acid solvent, using a perchloric acid catalyst, and then decomposing the methoxytricyclohexylidene peroxide product.

Monosubstituted macrocyclic compounds have been prepared with alkyl, aryl, acetoxy, benzoyloxy, halogen, and amido substituents.

The decomposition of the ketone peroxides is hypothesized by Dr. Story to proceed through homolysis of an oxygen-oxygen bond. The cleavage should be analogous to that of alkyl peroxides and ozonides, he believes, with a double β scission following homolysis of the oxygen-oxygen bond, producing alkyl radicals—which undergo a very efficient cage recombination to form a new carbon-carbon bond. An intermediate acyl peroxide is formed, and the cyclic hydrocarbon results from its homolytic decomposition, loss of carbon dioxide, and cage recombination of the resulting alkyl radicals. Preliminary data obtained on the kinetics, solvent effects, and activity parameters of the reaction are in support of this scheme.

The ketone peroxide fragmentation procedure already constitutes the most generally useful synthesis of macrocyclic systems. Dr. Story and his colleagues are currently seeking to extend the utility of the method to synthesis of very large ring systems—up to C_{100}, if possible—opening the door to study of many interesting conformational problems, and possible use of C_{30} to C_{40} rings as selective ion-chelating agents. They are also planning to apply their techniques to synthesis of heterocyclic ring systems and macrolide antibiotics. A further possible application is preparation of new monomeric systems for polymerization—using small or large rings as polymer monomers—yielding elastomeric materials which are elastic on a molecular basis because of ring rigidity.

Lead aerosol concentrations show seasonal variations

	Jan.-March	April-June	July-Sept.	Oct.-Dec.	Yearly mean
	Concentrations in micrograms/cubic meter				
1967					
Downtown	3.50	1.16	1.04	2.95	2.16
Mission Valley	—	—	1.07	1.87	—
Scripps Pier	—	—	0.27[a]	0.61	—
1968					
Downtown	3.27	1.13	1.33	3.65	2.38
Mission Valley	1.76	1.27	1.55	2.94	1.90
Scripps Pier	0.58	0.24	0.25	0.61	0.42
Laguna Mountain	—	—	—	0.04	—
1969					
Downtown	2.57	1.05	1.07	4.05	2.20
Mission Valley	2.05	1.48	1.52	3.14	2.06
Scripps Pier	0.40	0.21	0.23	0.63	0.37
Laguna Mountain	0.01	0.06	0.07	0.05	0.05

[a] Last six weeks of quarter.

cloudy with overcast mornings along the coast. Temperatures increase inland where skies are clear, creating a thermal low-pressure region in the interior and setting in motion summer sea breeze circulation. Therefore, lead concentration in the inland atmosphere is lessened by dilution with clean marine air. During winter months there is little difference between land and sea temperature and so sea breezes are diminished; the reduced wind velocity can't effectively dissipate pollutants, and lead aerosols accumulate in inland air.

Furthermore, during early mornings of winter months inversions develop when the wind is light and air layers above ground are dry, a situation contributing to rapid heat losses from the ground into the overlying air. Under these conditions the lowest temperature is found near the ground, and upward diffusion is inhibited. As a result, pollutants are trapped in a limited air space. During such inversion phenomena, the Chow group encountered high atmospheric lead content, especially at the downtown station. Weekly average lead concentrations as high as 8 micrograms per cubic meter have been observed downtown, says Dr. Chow. The tentative national air quality limit for lead is 10 micrograms per cubic meter as set forth last year by the American Industrial Hygiene Association.

Isotopes. Dr. Chow stresses that each lead ore deposit has its characteristic isotopic composition, which is fixed during mineral genesis, and it is this unique chemical property which he uses in identifying the source of industrial lead pollutants. Dr. Chow and his coworkers purchased various brands of gasoline from San Diego service stations and simultaneously gathered lead aerosol samples. They also obtained gasoline and aerosol samples from other cities. They then extracted the lead in the gasolines and aerosols and determined their isotopic compositions. They also determined the isotopic composition of lead in marine sediments and water.

They find that the isotopic composition of lead in gasoline additives and in aerosols represents a typical tertiary, or older age, mined ore lead which is less radiogenic than that of quaternary lead (which typifies the results of natural weathering). Marine sediments are also quarternary lead. This means that lead aerosols couldn't be derived from the surface soils by natural weathering, says Dr. Chow. Comparison of the isotopic composition of lead in the southern California aerosols with that of the averages of local gasoline leads shows that the two kinds of lead are identical within experimental error. This is true for other cities in the study, says Dr. Chow, indicating that excess lead in the aerosols can be attributed only to automotive exhausts.

What happens to lead aerosols in the atmosphere? In other studies, Dr. Chow finds that coarse fractions settle out along roadsides and account for high lead concentrations in soil and vegetation. Fine lead aerosols are able to travel long distances and are often washed out of the atmosphere in rain and polar snow. Part of the pollutants has been discharged directly or through runoff into the oceans.

Purity determination by DSC gain in accuracy

ANALYTICAL

Careful control of experimental variables can greatly improve the accuracy of purity determinations with differential scanning calorimetry (DSC). Using Perkin Elmer's DSC-1B instrument, Dr. Edward M. Barrall, II, and Richard D. Diller of IBM Research Laboratory, San Jose, Calif., have found that when they properly control all variables, they can obtain an accuracy of ± 3% of the low-concentration component. Dr. Barrall spoke at a symposium on recent advances in thermal analysis.

In differential thermal analysis (DTA), a sample's actual temperature change is measured (during an exothermic or endothermic reaction) as the sample is being heated or cooled. In DSC, the power required to prevent such a temperature change is measured.

In the operation of a Perkin-Elmer DSC instrument (C&EN, Aug. 18, 1969, page 46), an average temperature loop compares the average temperature of the sample and reference holders to what the linear programing unit directs. The loop controls the power to compensate for any deviation the sample and reference holders show from the heating program. As the temperature of the two holders is programed up or down, the program temperature analog is recorded on the x-axis of a strip-chart recorder.

Meanwhile, a differential temperature compares the temperature of the sample holder and the reference holder and proportions power to the heater in each holder so that the temperatures remain equal. When a sample undergoes an endothermic transition and melts, a differential temperature amplifier senses the heat lost by the sample holder and increases power to the sample holder to maintain thermal balance with the reference holder. A signal proportional to the power difference is plotted along the y-axis. In the resulting thermogram, the area under the curve measures the heat of transition directly in calories.

Applications. Purity determinations using DSC have been demonstrated by other workers, Dr. Barrall points out. For example, Dr. G. L. Driscoll, Dr. I. N. Duling, and Dr. F. Magnotta of Sun Oil Co., Marcus Hook, Pa., have used the technique to determine the mole fraction of impurity in several synthetic mixtures. And Dr. N. J. DeAngelis and Dr. G.

J. Papariello of Wyeth Laboratories, Randor, Pa., have tested the method on known samples of certain pharmaceutical materials, but found that it has certain limitations.

Although the DSC method shows promise in purity determination, little work has been done in examining the systematic variables and optimizing the conditions, Dr. Barrall says. Also, he and Mr. Diller recognize the need to compare analytical results obtained from the DSC method with other established analytical techniques.

In a purity determination, the DSC instrument is used to obtain a heat uptake-temperature curve in the heating mode. Given the proper conditions the melting curve has all the information needed to calculate the mole fraction of impurity using the van't Hoff equation. The van't Hoff equation, which relates melting point depression to impurity content, can be written as $T_s = T_o - RT_o^2X/\Delta H \cdot 1/F$ where T_s is the instantaneous temperature of the sample in °K., T_o is the melting point of the infinitely pure sample (solvent) in °K., R is the gas constant (1.987 cal. per mole-°K.), ΔH is the heat of fusion of the sample (solvent) in cal. per mole, X is the mole fraction of impurity, and F is the fraction of the total sample melted at T_s.

A plot of T_s versus 1/F theoretically gives a straight line with a slope of $-RT_o^2X/\Delta H$ with an intercept of T_o. ΔH can be obtained from the area under the DSC curve. T_s is measured from the DSC curve. 1/F is the reciprocal of the partial area of the DSC curve up to T_s divided by the total area of the curve. This particular correction has been recognized by many workers.

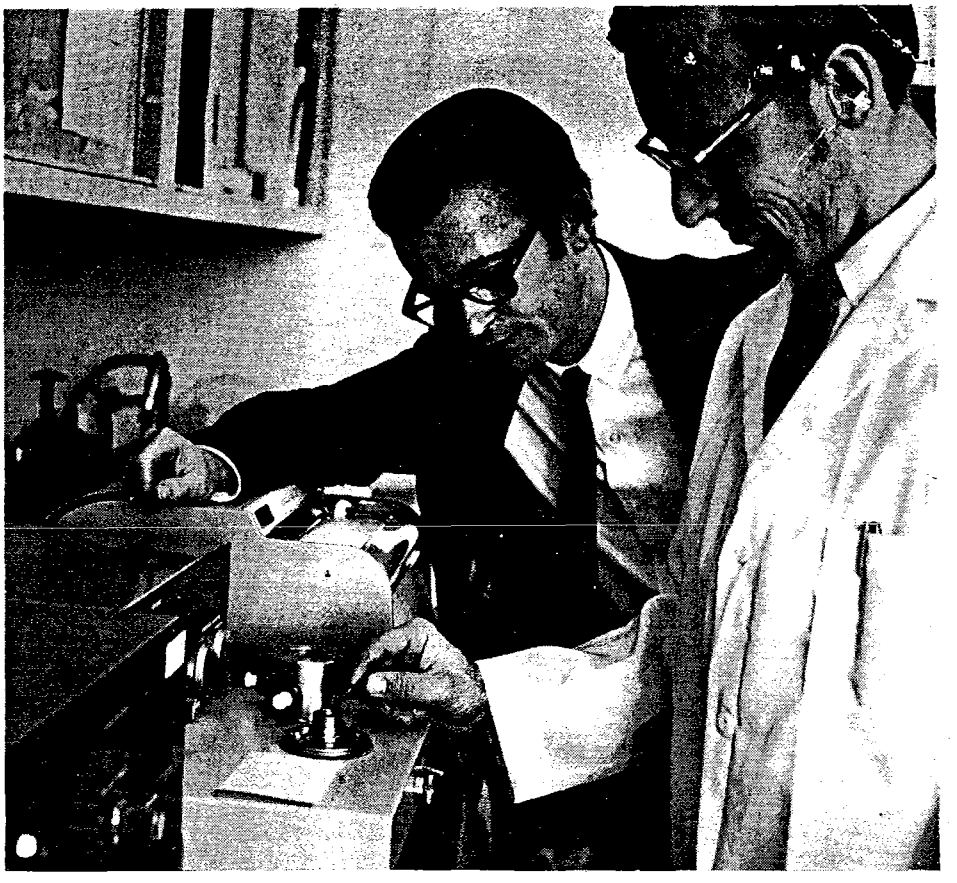
To use the van't Hoff equation in DSC purity determinations, a chemist must make sure that the impurity is insoluble in the predominant solid phase. Also, the impurity must be completely soluble (form an ideal solution) in the molten or liquid phase. The equation can't be used for cocrystals (impurity crystallizing in the host lattice), cases where the impurity forms a nonideal solution in the melt by association or chemical reaction, and cases where the impurity is totally insoluble in the liquid phase.

Corrections. To get accurate purity determinations with DSC, two corrections must be made to account for instrumental variables, the IBM chemists find. The first of these variables is thermal resistance of the instrument. This causes an error in the instrument's temperature reading. To correct for this, they melt a material of very high purity (greater than 99.999%) and record the melting curve. The pure material must melt in or near the range for which it is being used as a correction if the effective thermal resistance is to be evaluated completely. The curve's leading edge slope is directly proportional to the thermal resistance.

To correct any temperature in a recorded transition it's necessary to superimpose this slope on the curve and extrapolate to the isothermal base line. The standard curve must be obtained at the same chart speed, sensitivity, encapsulation, and heating rate as the purity determination of the sample.

The second instrumental variable for which a correction must be made is undetected melting. If the DSC is set at a sensitivity low enough to keep the whole record on the chart, the low temperature melting will not be detected by the recorder. This means that area will be lost, and the initial small fraction melted, F, will be too small.

This small amount of heat can be recovered by making the T_s versus 1/F plot linear, the IBM pair has shown. They do this by computer trial and error using progressively larger area increments to be added and determining the effect on the plot. The increment added to produce a linear plot is selected for the correlation. In addition, it's necessary to consider the entire endothermal area up to the vertex. This follows from the van't Hoff equation which describes the entropy of solution and mixing in the total liquid phase. It isn't necessary to have some arbitrary cutoff point as thought before.



Dr. Edward Barrall (left) and Richard Diller use DSC for purity determinations

Experimental. In the IBM studies on purity determination using the Perkin-Elmer DSC instrument, the data were reduced with a polar planimeter. The results were calculated with a computed program developed at IBM.

In their study, Dr. Barrall and Mr. Diller used samples in which the impurity could be analyzed by an alternate method. Among them were lead-tin, indium-lead, and tin-indium metal mixtures which were analyzed by atomic absorption spectrometry. The scientists studied organic mixtures which were analyzed by ultraviolet absorption spectrometry, fluorescence photometry, and thin-layer chromatography. These analyses were done on the sample that was thermographed. Serious impurity gradients can exist in a bulk sample, they found.

To obtain accurate, reproducible results in purity determinations, certain experimental precautions must be taken, the IBM chemists emphasize. Care must be taken that the sample doesn't relocate in the cell during fusion and freezing. This alters the thermal resistance between sample encapsulation and heater, changing the shape of the DSC curve inde-

pendent of purity. To keep the thermal resistance constant it's also necessary to position the sample pan in the same location in the calorimeter for each run.

The temperature of the sample is not a direct but a relative measurement in the DSC-1B instrument. Thus, it's necessary to calibrate the temperature axis. This is done with pure samples of metals or organic compounds melting in the range studied. The calibration is different for each heating range because the instrument's thermal resistance varies with temperature.

Equilibrium condition. Since the van't Hoff equation describes an equilibrium condition, the sample must be in equilibrium both physically and thermally at all times during the melting process in the purity determination. Physical equilibrium is promoted by using very small samples. Slow heating rates provide thermal equilibrium. With samples weighing 3 mg. or less and with a heating rate of 1.25° C. per minute, Dr. Barrall and Mr. Diller can get very good purity results. With a lead-tin mixture containing 0.419 mole % lead, they get an error of only about 1.4%.

When heating rates are above 1.25° C. per minute, or when sample mass is greater than 3 mg., the sample isn't at equilibrium during the entire melting process. Once melting exceeds a certain rate, Dr. Barrall explains, the calorimeter can't respond rapidly enough (because of the thermal resistance of the sample-encapsulation-cell combination) to record the process accurately. Thus, errors become more serious.

In high-impurity samples, eutectic formation can cause errors in purity determination by DSC. For example, in a sample containing 3.06 mole % stilbene in triphenylmethane, the IBM chemists found only 1.71 mole %. By contrast, with a sample containing only 0.71 mole % stilbene, they obtained 0.640 mole %, about a 10% error but still acceptable for most analyses. If the eutectic point is well removed from the melting points of either component, the error is small. However, if the eutectic melts within the low melting tail of the impure principal component, a serious error in the purity determination can result.

Materials which form cocrystals can be studied by DSC in some cases, the IBM workers say. But the van't Hoff method can't be used effectively with these materials. They find that they can construct a calibration curve based on endothermal minimum temperature as a function of the minor component concentration. This curve is very sensitive to purity at concentrations less than 5 mole % of impurity.

Pollution problems get assist from NAA of air

Technique determines composition of 33 elements in solid particles from air

ANALYTICAL

Neutron activation analysis (NAA) of particles carried by air will give investigators of air pollution an effective tool for understanding mechanisms of solids transport and discovering sources of pollution. These expectations were expressed by Dr. Richard Dams of Nuclear Research Center, Ghent, Belgium, speaking of work with Dr. John W. Winchester, Dr. John A. Robbins, and Kenneth A. Rahn done at University of Michigan, Ann Arbor.

The techniques used by the Ann Arbor men determine composition of 33 elements in solid particles collected from air. Applicability to arsenic, antimony, mercury, and selenium gives information vital to judging health dangers of air polluted by sizable amounts of these elements, says Dr. Dams. The method would have come in handy in the New York City-New Jersey area last month as officials sought frantically to find the source of a highly irritating miasma which wafted in no apparent pattern over New York City and several New Jersey communities. Dr. Dams sees the availability of profiles on so many elements as an aid to locating pollution sources by their compositional fingerprints.

The Michigan team collects particulate matter by drawing air at high flow rates through 25-mm. polystyrene filters. Purity of filter materials is important, since trace impurities give rise to high blanks in supersensitive neutron activation analysis. Even in their best work, however, chlorine is still a problem, and they report no results in a trial run of the method.

Irradiated. Placed in polyethylene, the filter is sent into the core of a nuclear reactor, where it is irradiated at a flux of 2×10^{12} neutrons per cm.^{2}-sec. for five minutes. The filter is removed from the polyethylene package and counted after three minutes with a Ge(Li) detector coupled to a 4096-channel analyzer. These instruments detect gamma rays at energies characteristic of each element. The count after three minutes gives quantities of isotopes with very short half-lives, such as those from calcium, titanium, vanadium, copper, aluminum, and sulfur. A second count on the same filter after 15 minutes, when very hot radioactivity has died away, allows determination of sodium, magnesium, manganese, indium, chlorine, bromine, and iodine.

A second irradiation at 1.5×10^{13} neutrons per cm.^{2}-sec. on the same sample gives analyses of longer half-life isotopes. A count after 20 to 30 hours gives potassium, lanthanum, samarium, europium, copper, zinc, tungsten, gold, gallium, arsenic, antimony, and bromine, whereas another count on the same sample after 20 to 30 hours assays scandium, cerium, thorium, chromium, iron, cobalt, nickel, silver, zinc, mercury, antimony, and selenium.

The Ge(Li) detector is a germanium crystal doped with gallium, which is then treated with lithium to allow that metal to diffuse into crystal interstices. The detector acts like a solid-state Geiger counter with gamma rays triggering generation of electrons and positive electron-holes, which then travel to the appropriate electrode attached to the crystal for detector current glow. The 4096 channels of the analyzer are stepped 1 k.e.v. apart in terms of gamma ray energies, and the rise and fall of a peak in the spectrum is interpreted by an IBM system 360/67 computer, which reads the intensity in each channel.

Routine. The FORTRAN IV program enables the computer to analyze peak shapes for discrepancies, do qualitative and quantitative analysis for the 33 elements based on counting rates in each channel—stored on seven-track magnetic tape—and subtract analytical blanks. The reactor and computer systems are quite sophisticated, but the Michigan scientists see the collection of samples as easily teachable routine.

The only disquiet the scientists express is dwindling of sources of pure polystyrene filter materials. Their present stocks were obtained from a firm in Germany which has since stopped making material in such high purity. Dr. Winchester is presently trying to generate interest in commercial production of high-purity polystyrene filters for air monitoring.

Dr. Andrews (front) and Dr. Boss study algebraic structure of genetic code

DNA code may transmit "superinformation"

Redundancy enables codons to do more than pick amino acid sequence in proteins, Florida team says

PHYSICAL

Scientists should look for "superinformation" in the algebraic group structure of the genetic code, according to Dr. Donald H. Andrews and Dr. Manley L. Boss of Florida Atlantic University, Boca Raton, Fla. In codes used for electrical transmission of engineering signals, they note, group structure is imposed to increase efficiency and reduce error. Similarly, they reason, the group characteristics of codon redundancy could serve to transmit additional information superimposed on the messages directing amino acid order in protein synthesis.

Dr. Andrews, a chemist, is distinguished professor of biophysics at Florida Atlantic. He and Dr. Boss, chairman of the biology department at the same school, are studying algebraic group correlations of activation entropies controlling chemical transference of information.

Discussing the team's findings, Dr. Andrews notes that the molecules that serve as carriers of genetic information control the reaction involved in protein synthesis by acting as catalysts. But, he maintains, the function of these catalysts is not primarily to change the activation energy; rather, they influence the rates of reactions by changing the activation entropy.

Barrier. The relation between entropy and chemical transference of information can be shown in the simpler types of state change found in crystal growth, Dr. Andrews explains. The simplest type of crystal growth takes place when molecules in a supercooled liquid are oriented and attached to the surface of a crystal immersed in the liquid. If there is no seed crystal, the supercooled liquid can remain liquid for months. The kinetic barrier is high enough to keep the crystallization rate infinitesimally small, Dr. Andrews observes. The barrier—the activation free energy for the reaction—is much higher than the barrier for normal growth because of the absence of any crystal surface.

A large positive value for activation free energy means that there is a large negative value for activation entropy, Dr. Andrews continues. Because of the relation between entropy and information, he adds, one can say that a large amount of "information" is needed for the reaction to proceed when the activation entropy has a large negative value. The "ignorance barrier" is very high, Dr. Andrews comments.

But when a single seed crystal is added, the supercooled liquid starts to crystallize on the surface of the seed crystal. Addition of the seed crystal provides the "information" which lowers the "ignorance barrier," Dr. Andrews says. The probability of the reaction increases, activation entropy is raised, the free energy barrier is lowered, and growth proceeds rapidly.

Crystallization can often be induced by seeding with a different substance or even by scratching the side of the container. In such cases, Dr. Andrews says, the equivalent of introducing a smaller amount of information.

Similarly, entropy of activation is also directly related to molecular symmetry, Dr. Andrews continues. For example, benzene has a symmetry number of 12: There are 12 equivalent positions as the molecule is rotated and inverted, 12 ways for the molecule to fit into a crystal lattice. Benzene's melting point is about 5° C. In contrast, the structurally similar but asymmetric 1,3-cyclohexadiene (symmetry number = 1) has about the same heat of fusion as benzene, but melts at −89° C. The difference in melting points—and entropy—is functionally related to the difference in symmetry, Dr. Andrews states.

Group. Transformations of the position of a benzene molecule from any one position to any of the 12 possible equivalent positions constitute an algebraic group. The symmetry number is the number of elements in the group. Since the symmetry number affects activation entropy, and since the order of the group is numerically equal to the number of elements in it, Dr. Andrews says, the activation entropies for a set of similar molecules having different symmetries are functionally related to the order of the groups involved.

As in crystal growth, a major process in biological growth is the transfer of molecules from a state resembling a liquid to a state resembling a solid. If algebraic group relations play a role in crystal growth, Dr. Andrews asserts, it should not be surprising to find them also playing a role in biological growth.

Protein synthesis, the basic process in biological growth, is controlled by the genetic code expressed by the order of nucleotides in deoxyribonucleic acid (DNA). The genetic code is redundant and, Dr. Andrews says, the redundancy has group characteristics. In the case of a symmetric molecule, the algebraic group consists of all possible transformations of position. In the genetic code, the "positions" consist of all possible forms of the codons which code for the different amino acids.

Codons. Consider, Dr. Andrews says, one of the codons found in messenger ribonucleic acid (mRNA), an intermediate between DNA and protein. UUU is one of the codons for phenylalanine. This codon can be changed into all the other possible codons, he explains, by inserting into each of the three places in the codon one of the four symbols U, A, C, or G (corresponding to the RNA bases uracil, adenine, cytosine, and guanine). Since there are four possibilities for each of three places, there are $4 \times 4 \times 4$ possible codons.

When the Florida workers arranged the 64 codons to show their algebraic group relations, they also uncovered