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Measurement of Some Potentially Hazardous Materials in the Atmosphere of Rubber Factories

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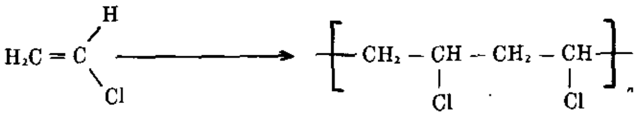
Two separate topics of work are outlined: methods for the measurement of chlorinated monomers in PVC and polychloroprene, and also methods for the measurement of these materials in factory air. Typical results which have been obtained in supplies of raw materials, in finished products, and in the working atmosphere at manufacturing operations are given. The second topic concerns the measurement of benzo[a]pyrene in the atmosphere of a tire manufacturing plant. This material is present in trace quantities in the mineral oils and carbon blacks used by the industry. The atmospheric concentrations present at various processes in this plant were measured on a daily basis over a period of two years, and the results obtained compared with results taken concurrently from an outside air station. It is shown that no significant quantities of benzo[a]pyrene are produced by tire manufacturing operations.

It is arguable that the rubber industry uses a greater variety of chemicals than any other single sector of industry. For instance, well over a thousand different raw materials, other than the polymers themselves, are currently listed for use by my company. Furthermore, because a great many of the processes used by the industry cannot easily be automated these chemicals cannot be handled in closed systems. For these reasons, it is vitally important that the industry monitors very closely the materials which it is using, not only in the sense of knowing what they are, and what impurities are present in them, but also in knowing how much of these materials are present in the factory atmosphere.

In the U.K., because of the historical and tragic experiences with bladder cancer, the industry is very aware that the problems in this area are not just abstract exercises brought about by the current popularity of environmental issues, but that unless a continuous vigilance is maintained there can be real hazards striking at the health of large numbers of people working in the industry.

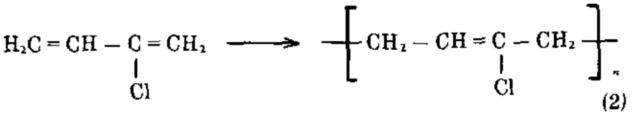
This paper outlines two separate topics of work recently carried out in this field. The first concerns chlorinated monomers from PVC and polychloroprene, and the second involves benzopyrene measurements in factory air.

It is now well known that some workers who have been exposed to high concentrations of vinyl chloride in the production of PVC have developed liver cancer. However, other unsaturated chlorinated monomers are used to make polymers, and some of these have been reported to be likely to have similar effects to vinyl chloride. One of these is chloroprene, used to make polychloroprene (Neoprene). Equations (1) and (2) show how this is related to PVC.



$$H_2C=\overset{H}{\underset{Cl}{C}} \longrightarrow \left[CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH} \right]_n$$

Vinyl Chloride   Poly(vinyl Chloride) (1)



$$H_2C=CH-\underset{Cl}{C}=CH_2 \longrightarrow \left[CH_2-CH=\underset{Cl}{C}-CH_2 \right]_n$$

(2)

Chloroprene   Polychloroprene (Neoprene)

Both PVC and polychloroprene are widely used by the rubber industry, and it has therefore been necessary for the industry to measure

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how much monomer was present in the polymers they were buying, and what concentrations of these monomers were present in the factory atmospheres.

Monomer in Polymer

A similar technique was used for both polymers. A weighed sample of the polymer was dissolved in a solvent, and a measured amount of the solution injected onto the gas chromatograph. The size of the peak obtained was then compared with peaks produced from calibration solutions containing known amounts of the monomer. An internal standard in the solvent was used to check on the quantity of solution introduced onto the chromatography column. The results of this are shown in Table 1, the figures given being in parts per million by weight of the polymer. The quantity of monomer in the PVC samples has been generally reduced by the manufacturers since the quoted results were obtained.

Table 1. Vinyl chloride in PVC.

Raw PVC	VC in PVC, ppm
New supplies, various manufacturers (1974)	100–200
Older supplies, various manufacturers (1974)	5–50

The same technique can be used to measure the residual monomer in finished products, and Table 2 shows some results of this. Very little monomer remains in these finished products, showing that most is released during processing.

Table 2. Vinyl chloride in manufactured products.

Product	VC, ppm
Golf shoe, sole	0.5
Golf shoe, upper	None detected
Wellington boot, sole	0.8
Wellington boot, upper	0.9
Shuttlecock head	None detected
Fire hose	0.6
Floor tiles	None detected
Food Grade PVC conveyor belt	None detected
Irrigation hose	0.6
Oil seals	None detected
PVC floor decking	None detected
PVC/nitrile molding	None detected

For polychloroprene, there is a negligible amount of monomer present in the solid material (Table 3), but quite large amounts of monomer are present in the latex, and this can generate high concentrations in the head space above the liquid.

Table 3. Chloroprene in polychloroprene.

	Chloroprene, ppm
Solid polychloroprene	<1
New samples of polychloroprene latex	4000–5000
Old samples of compounded polychloroprene	1500–2000
Atmospheric concentration in air space in a closed vessel of polychloroprene latex	800–1500 (v/v)

Monomers in the Working Atmosphere

Many techniques now exist for carrying out these measurements. The method used here involves absorption of the monomers on activated charcoal and subsequent analysis by gas chromatography. This has the advantage that it can be used for most monomers, and is specific and quite sensitive.

Air is drawn through activated charcoal by means of a battery-operated sampler (Fig. 1).

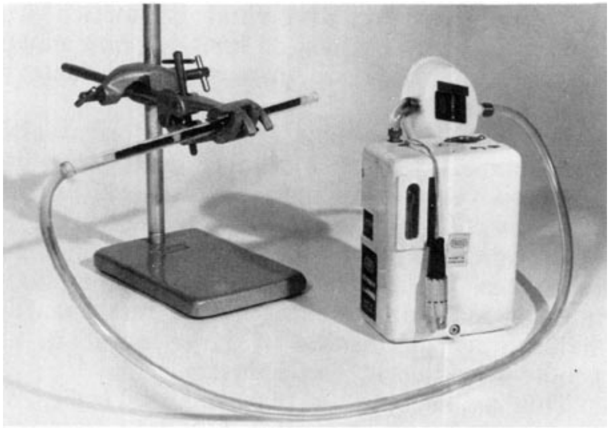

FIGURE 1. Sampling equipment for monomers.

This apparatus can be used statically, or is small enough to be carried by a workman during his normal operations, thus giving an accurate assessment of the concentrations to which he is exposed. The charcoal is contained in a small glass tube measuring 20 cm × 0.5 cm diameter, (Fig. 2) and is divided into two segments, separated by quartz wool plugs. This enables a check to be made that the charcoal has not been overloaded. In nearly all cases, sampling can be arranged so that all the monomer is trapped on the first charcoal segment, and none should be detectable on the second. After sampling, the tube is sealed and taken back to the laboratory. The trapped monomer is then desorbed from the charcoal into a solvent (usually carbon disulfide) and the solution measured on the gas chromatograph. The overall efficiency of the method was checked by sampling known concentrations of monomer prepared in large polythene containers and was shown to give better than 90% overall recoveries.

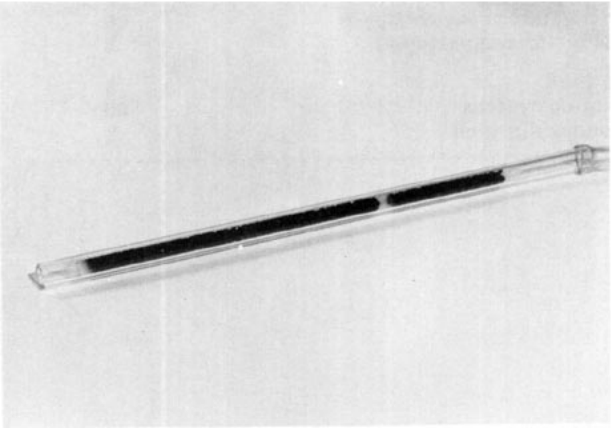

FIGURE 2. Charcoal absorbing tube for monomers.

Table 4 shows the results obtained for vinyl chloride in factory atmospheres. PVC is used in a total of ten Dunlop UK factories, the main products being floor tiles, footwear, and conveyor belting. The highest concentration found was close to a heated high-speed PVC mixer, where a reading of 23 ppm (v/v) was obtained. This mixer was subsequently totally enclosed and fitted with exhaust extraction, and factory flor concentrations reduced to less than 1 ppm.

Table 4. Atmospheric vinyl chloride concentrations.

Product	Location	VC, ppm
Floor tiles	Banbury mixer	<0.1
	Calender	<0.2
	Stores, close to sacks	0.7
	Printing roller	0.4
Footwear	Heated high speed mixer	23
	Heated high-speed mixer after totally enclosing and fitting extraction	<1
	Over center of cooling chamber	1.4
	Over chute from mixing platform to cooler	0.6
	Injection molding machines	<0.2
Belting	Mixing platform	<0.2
	Coating unit	<0.2
	Edging units	<0.2
Artificial tennis court surface		<0.2
Fire hose	Coating and heating units	0.3
	Extrusion unit	0.2
Oil seals	Production units	<0.2
	Stores, close to sacks	4
Badminton shuttlecocks		<0.2
Precision moldings		<0.2
Floor decking		<0.2

The British Rubber Manufacturers' Association recommends its members who process PVC to maintain atmospheric concentrations below 1 ppm, and this condition is met in all Dunlop factories.

Table 5 gives results obtained during work with polychloroprene latex. This material is used in flooring applications, and for making dipped goods. The current threshold limit value for chloroprene is 25 ppm, and this value was not reached even in confined conditions. However, all these operations were carried out at room temperature, and if the raw latex is heated, excess concentrations could result.

This work is currently being extended to the measurement of vinylidene chloride, styrene, and acrylonitrile monomers.

Benzo[a]pyrene in Tire Factory Atmospheres

Benzo[a]pyrene (B[a]P) is present in trace quantities in the oils used by the rubber industry as raw materials. Over 20% of a modern car tire consists of mineral oil, and the oils used

Table 5. Atmospheric concentrations of chloroprene.

	Location	Chloroprene, ppm
Manufacture of flooring materials: *open factory area*	Mixing polychloroprene latex with other additives	3
	Above drum of compounded latex during dispensing into smaller containers	2
	Above main mixer during stirring and dispensing into smaller drums	12
Application of flooring material in confined areas (on board ship)	Personal sample (spreading operative)	4
	Personal sample *(mixing operative)*	2
	Static sample in confined cupboard space	6
	Static sample, center of compartment	3
Production of dipped goods from polychloroprene latex	Rear edge of dip tank	2
	During topping up operations	20
	Over hot water bottle dip tank	2

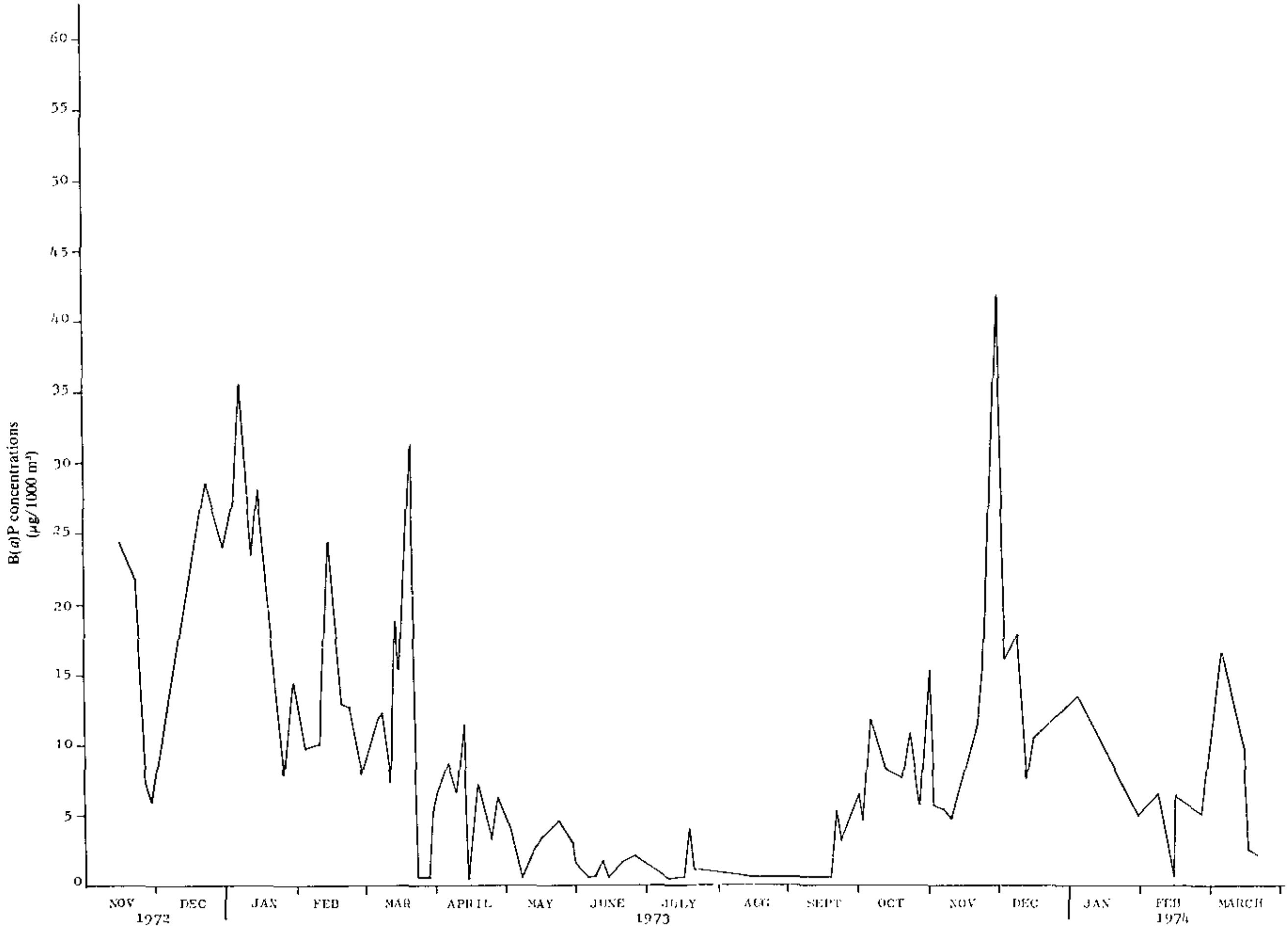

FIGURE 3. Benzo[a]pyrene levels in Birmingham air.

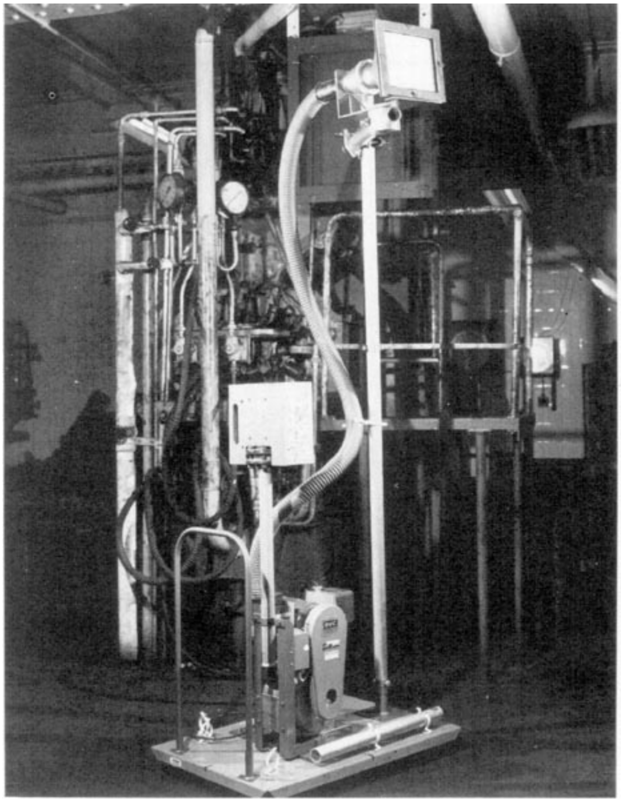

FIGURE 4. High volume air samples, arranged for high sampling positions.

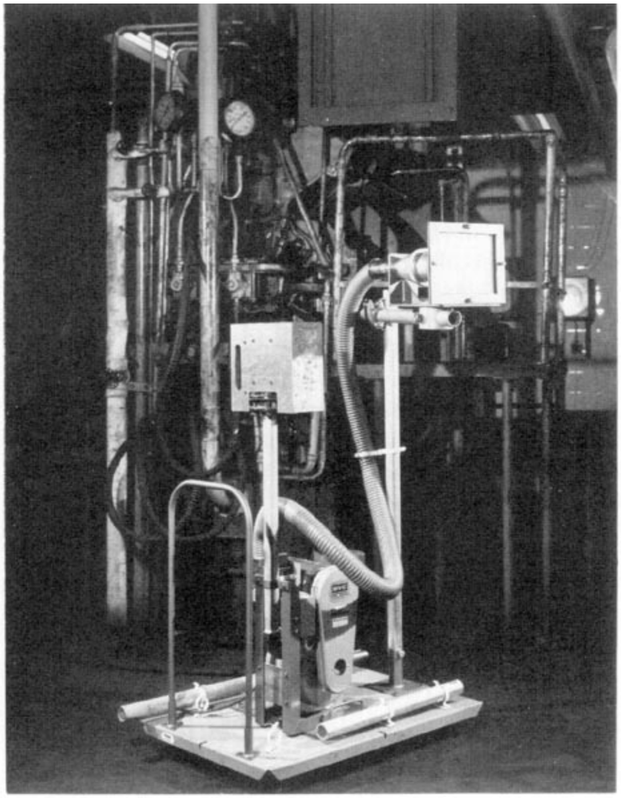

FIGURE 5. High volume air samples, arranged for low sampling position.

are often the high boiling aromatic type in which the amounts of polycyclic aromatic hydrocarbons present are expected to be higher than overage. B[a]P and other polycyclic aromatic hydrocarbons also occur in trace quantities on the surface of the carbon blacks used by the industry.

The British Rubber Manufacturers' Association has been carrying out a large scale epidemiological survey of health in the UK rubber industry, and as part of that survey we have attempted to find out whether any of the B[a]P contained in the oils and carbon blacks is released to atmosphere during processing.

B[a]P is produced whenever fossil fuels are burned and so is present in small concentrations in urban air. The concentration of B[a]P present in the ambient air at Dunlop Research Centre, Birmingham, was measured on a daily basis over a period of 2 yr. This sampling site is in a mixed suburban/industrial area, and is situated approximately 1 km from a main motorway. The concentrations measured are shown in Figure 3. The data show the seasonal variation which has been previously noted for polycyclic hydrocarbons in urban air, with values up to 40–50 ng/m^3 in winter, and much lower values, down to 1–5 ng/m^3 or less in summer. The graph also shows that fairly sharp changes in B[a]P levels occur over a shorter time scale of a few days. Some evidence exists to show that the high temporary concentrations of B[a]P shown on the graph are associated with atmospheric temperature inversions (*1*).

The amounts of B[a]P measured here are very small—about one millionth of the amounts normally involved in the measurement of threshold limit values. Consequently, in order to obtain sufficient material for analysis, it is necessary to take a very large sample of air of the order of 1000 m^3. It is possible to obtain commercial high volume samplers which will give a sample of this size in a day, but it was found that these were not well suited to sampling in factories. The major problem here is that in the more contaminated factory atmospheres, a large sample builds up on the filter which is being used and cuts down the air flow through the sampler. This not only reduces the size of air sample obtained, but since these samplers rely on the air flow to cool the motor, these burn out very rapidly. To eliminate this type of problem, a large trolley-mounted sampler was designed in which the pump was driven separately from the motor (Figs. 4 and 5). The filters on these samplers were remotely mounted on a scaffolding system to enable them to be positioned at the point of interest.

It has previously been shown that all the B[a]P present in air is absorbed onto solid particles and so can be completely removed by filtration (*2*). This was confirmed by including a pre-extracted activated charcoal filter behind the main glass fiber filter. It was shown that all the B[a]P collected was present on the main glass fiber filter and that none could be detected on the charcoal absorber.

Having collected the sample, the filter was extracted with cyclohexane in a Soxhlet apparatus and the solution concentrated and fractionated by column chromatography on partially deactivated alumina. The fractions were then examined for B[a]P by means of ultraviolet spectroscopy. This type of analysis has now been in use for a considerable number of years (*3*), but it was found that because it was possible to handle relatively large quantities of fairly heavily contaminated samples, it was more suitable for this type of factory examination than many of the more recently developed methods.

Samples were taken at 49 sites inside a tire manufacturing plant, each sample being taken over a period of 2 days.

Concurrently, samples of the outside air were taken at a station about 1 km from the factory. Typical results are shown in Table 6. The results for outside air obtained over the same 2 days as the factory samples are given for comparison. For the 49 factory sites measured, the mean of results in which a measurable concentration of B[a]P was found was 12.3 ng/m^3. The mean of the corresponding results in the outside air was 11.6 ng/m^3. The difference between these results is not statistically significant at the 90% level.

Table 6. Benzo[a]pyrene in factory air.

Site	B[a]P, ng/m^3	
	In factory air	Outside air
Transfer mix	19.0	16.6
	16.7	11.5
	Not detectable	9.8
	6.5	2.5
Above extruder	3.2	6.4
	7.9	4.6
	7.3	11.9
	6.0	8.3
Above extruder	8.4	8.3
	5.0	7.6
	12.1	10.9
	8.5	10.9
Tube department	21.3	11.4
Above conveyor	15.7	15.5
	43.0	41.8
	18.8	16.1
Tube department	32.1	41.8
Joining section	Not detectable	16.1
	8.7	7.5
	14.6	10.5
Tire curing presses	7.9	10.9
	12.8	15.1
	5.3	5.9
	3.7	5.4
Tire curing presses	9.5	10.9
	9.5	15.1
	3.7	5.9
	4.0	5.4
63½-in. Bagomatic presses	2.2	6.4
	6.1	4.1
	11.1	11.9
	7.0	8.3
Tire trimming area	23	27.4
	2.2	7.9
	16.2	14.4
	6.4	24.3
	13.4	11.6
	13.5	7.4
	22	18.8
	54	12
	56.8	12
	Not detectable	13
	Not detectable	7.4
	Not detectable	15.4

It is possible to estimate the amounts of B[a]P which might be considered significant by comparison with other situations. The B[a]P concentrations in gas works retort houses in the U.K. in the early 1960's was in the range 1400–4800 ng/m^3 (*4*), and in coking plants in Czechoslovakia was reported to be in the range 300–35,000 ng/m^3 with an average value 400 m from the ovens of 1800 ng/m^3 (*5*). Clearly, the amounts of B[a]P present in a tire factory are far less than these figures. For urban air, the National Academy of Sciences report on particulate polycyclic organic matter in (*6*) showed that B[a]P could to some extent be used as a "marker" for urban air pollution, and that each increment of 1 ng/m^3 B[a]P could be correlated with a 5% increase in lung cancer death rate. Obviously this argument is not directly applicable to the industrial situation, but it can be seen from the above figures that even with this criteria, no significant excess of B[a]P has been recorded in this series of measurements. It can therefore be clearly stated that the B[a]P which is present in some of the raw materials used by the rubber industry is not released to atmosphere during the processes of tire manufacture.

REFERENCES

1. Willoughby, B. G. Report on the Monitoring of the Atmospheric Environment in U.K. Tyre Manufacturing Work Areas. Rubber & Plastics Research Association, Great Britain, 1975.
2. IARC Working Group on Air. Standardisation of sampling and analytical procedures for estimation of polynuclear aromatic hydrocarbons in the environment. International Agency for Research on Cancer, Geneva 1969. Internal Technical Report 71/002, Appendix V, p. 5.
3. Commins, B. T. A modified method for the determination of polycyclic hydrocarbons. Analyst 83: 386 (1958).
4. Lawther, P. J., Commins, B. T. and Weller, R. E. A study of the concentrations of polycyclic aromatic hydrocarbons in gas works retort houses. Brit. J. Ind. Med. 22: 13 (1965).
5. Masek, V. Benzo[α]pyrene in the workplace atmosphere of coal and pitch coking plants. J.Occup. Med. 13: 193 (1971).
6. U.S. National Research Council (Division of Medical Sciences) Committee on Biologic Effects of Atmospheric Pollutants. Particulate Polycyclic Organic Matter. National Academy of Sciences, Washington, 1972, p. 246.