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# The Effect of Filter Pore-Size on Analytical Concentrations of Some Trace Elements in Filtrates of Natural Water

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Silver metal (Flotronics) membrane filters (pore-sizes 5–0.2  $\mu\text{m}$ ) and cellulose ester (MF-Millipore) membrane filters (pore-sizes 5–0.025  $\mu\text{m}$ ) are used to elucidate the relationship between filter pore-size and analytically determined concentration of total “dissolved” iron, aluminium, silicon, and magnesium in the resulting filtrates. Iron and aluminium concentrations in the filtrate decrease with decreasing filter pore-size, but silicon and magnesium remain constant with changing filter pore-size. Filtration with two different types of membrane filter under the same conditions and having the same nominal pore-size produces differences in analytical concentrations of iron, aluminium, and silicon in the respective filtrates. This reduction is due very likely to a more complete removal of particulate matter by metal membrane filters compared to Millipore filters of the same nominal pore-size.

Acidification of filtrate with hydrochloric acid produces some reduction in determinable iron and aluminium by flameless atomic absorption. The cause does not appear to be the volatilization of metal chlorides during the charring of the sample, but this remains to be investigated further.

A large sample of water, unpolluted by man, from the Arctic Red River, NWT, Canada, was used for these experiments.

**KEY WORDS:** Membrane filters, natural water, trace analysis, iron, aluminium.

## INTRODUCTION

It is generally recognized that particulate matter in the water sample and adsorption on these solids are two chief causes of analytical error in determination of trace elements in lake or river water samples. Particulate matter in the analytical sample was implicated as the cause of variation in the analysis of iron in sea water by Cooper,<sup>1</sup> Spencer and Brewer,<sup>2</sup> and Einsele.<sup>3</sup> The analysis of dissolved phosphorus in lake water by Chamberlain,<sup>4</sup> and

Rigler<sup>5</sup> and others showed that analytical concentration of "dissolved" phosphorus varied systematically with the pore-size of filters used to filter the lake water sample prior to analysis. In lake and river water the "dissolved" analytical concentration, at least in the case of phosphorus, is now recognized to be an operationally dependent quantity. In the case of iron, Lewis and Goldberg<sup>6</sup> had recognized the importance of suspended particulate matter as a possible contribution to analytically determined "dissolved" iron in marine waters, but they did not investigate systematically this problem. More information on the influence of some methodological variables such as filter pore-size on analytical concentration of species other than phosphorus is required not only for improving consistency and accuracy of analytical data in general, but also for better understanding of the mechanisms which control solubility and distribution of common trace elements in natural waters. Very little is known about the analytical concentration dependence on pore-size of species other than phosphorus in natural water. "Solution" concentration data which are based on an operational distinction between dissolved and colloiddally dispersed or particulate matter are useful and acceptable for certain applications, but are of limited value for thermodynamic calculations. This paper presents "solution" concentration data for iron, aluminium, silicon, phosphorus, and magnesium in a river water sample as a function of filter pore-size for two types of membrane filter: silver metal, and Millipore (mixed esters of cellulose).

## METHODS AND MATERIALS

### Sample description

Twenty liters of river water were collected in polyethylene carboys from the Arctic Red River at Martin House, NWT (66°47'18"W × 135°5'12"N) and from the Mackenzie River just upstream of Norman Wells, NWT (65°15'57"W × 126°49'24"N) respectively, on September 12, 1971. These bulk water samples were stored at 5°C for six months, and equilibrated for one month at room temperature prior to filtration and chemical analysis. The relatively long storage and equilibration times served to reduce changes in ionic concentration during the course of the experiments. The water samples contained suspended sediments of 74 mg/l and 55 mg/l in the Arctic Red River water and Mackenzie River water respectively.

### Filtration

Two kinds of membrane filters (of various pore-sizes) were used, MF-

Millipore (mixed esters of cellulose), 142 mm in diameter, of average pore-size 5  $\mu\text{m}$ , 3  $\mu\text{m}$ , 1.2  $\mu\text{m}$ , 0.8  $\mu\text{m}$ , 0.45  $\mu\text{m}$ , 0.2  $\mu\text{m}$ , 0.1  $\mu\text{m}$ , 0.05  $\mu\text{m}$ , 0.025  $\mu\text{m}$ ; and "Selas Flotronics" silver metal filters, 47 mm in diameter, of average pore-size 5  $\mu\text{m}$ , 3  $\mu\text{m}$ , 0.8  $\mu\text{m}$ , 0.45  $\mu\text{m}$ , 0.2  $\mu\text{m}$ . The pore-sizes quoted are those given by the respective manufacturers. A "Millipore, Teflon, 142 mm" filter holder and a stainless steel "MMH-47, Flotronics" filter holder were used with the two types of membrane filters. Nitrogen gas at 20 psi or less served as a pressure medium for filtration. Membrane filters were soaked prior to use in distilled, demineralized water acidified with hydrochloric acid to pH2, for approximately 24 hours, and then washed with 3 liters of distilled, demineralized water. For each filter the final 400 ml portion of this wash water was retained as a blank. Unless analysis of the blank showed that the filtration system itself produced no significant concentration for the species to be analyzed results were discarded and filtration was repeated. As an additional precaution the first 50 to 100 ml portion of river water filtrate from each membrane used was discarded. While the bulk river water was stirred with a teflon coated stirrer, a 500 to 550 ml subsample was withdrawn of which three 150 ml portions were filtered with each membrane and collected in three clean polyethylene bottles. One bottle was acidified with hydrochloric acid to pH 1.5, the other bottle was acidified to the same pH with nitric acid, and the third bottle was unacidified. Only high-purity ("Ultrex") acids were used.

### Analyses

Magnesium was determined directly by conventional flame atomic absorption spectroscopy using a Perkin Elmer Model 403 instrument. Machine settings and the analytical methods were those given in the Perkin Elmer methods manual "Analytical Methods for Atomic Absorption, March 1971". Silicate in solution was determined by the molybdate/stannous chloride method of Armstrong and Butler.<sup>7</sup> Total dissolved phosphorus (TDP) was determined as the orthophosphate by the method of Murphy and Riley<sup>8</sup> (molybdate/antimony/ascorbic acid), after UV-irradiation of the solution by the technique of Armstrong and Tibbits,<sup>9</sup> and Henriksen.<sup>10</sup> Spectrophotometric measurements were made with a Bausch and Lomb Spectronic 400 spectrophotometer. Iron and aluminium were determined directly in the filtrate without preconcentration or extraction, by the flameless atomic absorption method using an HGA 70 Perkin Elmer graphite cell unit and a Perkin Elmer Model 403 spectrophotometer. Analytical sample volumes of 50  $\mu\text{l}$  (injected with an Eppendorf pipette) were used, and the instrument was calibrated against standards prepared daily from 1,000 ppm stock solutions. The basic principles and operational techniques of the graphite tube analytical

method were described in detail by Massmann,<sup>11</sup> and Manning and Fernandez.<sup>12</sup> Papers by Paus,<sup>13</sup> and Kahn<sup>14</sup> deal with the application of this method to analysis of natural water for trace metals. Estimates of analytical precision for the methods and elements in question were established from separate experiments. The precisions for each element in terms of coefficient of variation are given in the following table:

TABLE I  
Analytical Precisions and Lower Limits of Measurements

Element	Coeff. of Var.		Range of Conc. to which Coeff. of Var. applies	Limit of Reliable Measurement <sup>a</sup>
	$\frac{s \times 100}{\text{Av. Conc.}}$			
	%			
Mg	2	10-15	mg/l	0.05 mg/l
Si	2	1- 4.5	mg/l	1 $\mu\text{g/l}$
TDP	34	7	$\mu\text{g/l}$	5 $\mu\text{g/l}$
Fe	4	50	$\mu\text{g/l}$	5 $\mu\text{g/l}$
Al	3	20	$\mu\text{g/l}$	5 $\mu\text{g/l}$

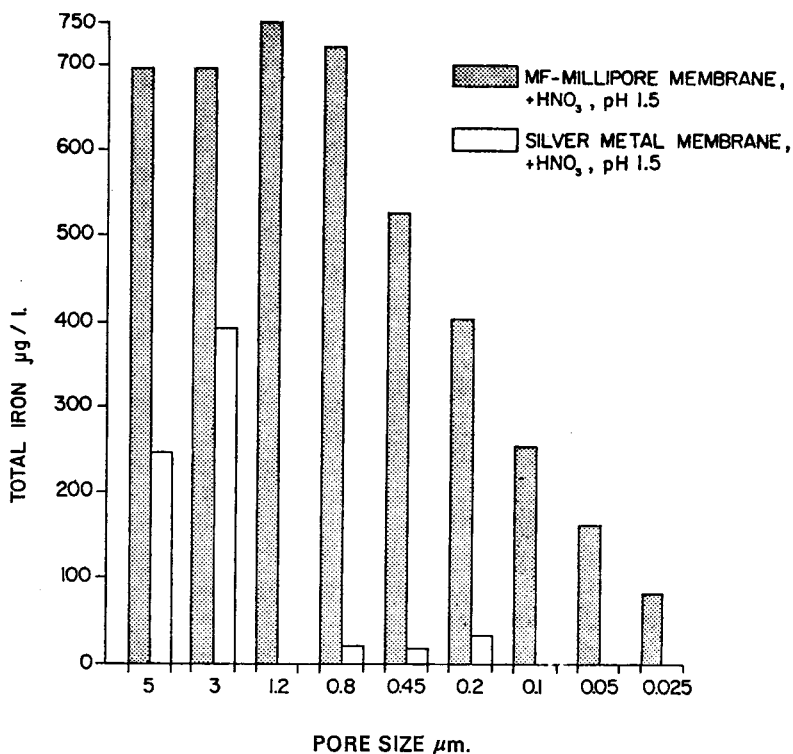
<sup>a</sup> Twice the standard deviation obtained from ten to twelve repetitive measurements near the respective lower limits.

## RESULTS AND DISCUSSION

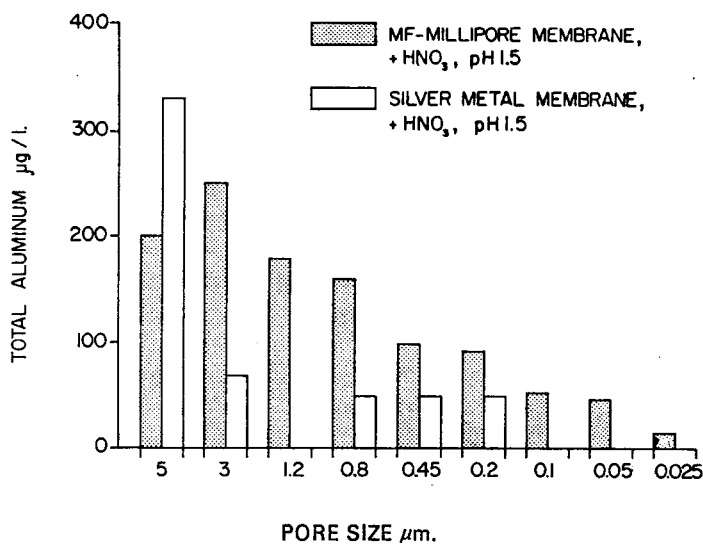
In Figures 1 and 2 are given the analytical concentrations of total "dissolved" iron, and total "dissolved" aluminium in acidified filtrates of a river water sample as a function of membrane filter pore-size, for metal and "Millipore" type membranes. Two findings are immediately apparent from these data:

- 1) For both types of membrane filter the analytical concentration of iron and aluminium, in the filtrate, depends on pore-size of the membrane,
- 2) The analytical concentration of iron and aluminium in a filtrate obtained with a metal membrane of a certain pore-size is generally lower than in a filtrate obtained with a Millipore membrane of the same nominal pore-size.

Since the discussion that follows is based on the contention that observed changes in analytical concentrations of chemical species are related to filter pore-size, it is appropriate to state at the outset the facts in support of this contention. The analytical precision for each element determination was established in separate experiments, Table 1. Changes in analytical concentrations of iron and aluminium which arose concomitantly with a change in



**FIGURE 1** Dependence of analytically determined total iron in filtrates of river water upon filter pore-size for Millipore and metal membrane filters. Filtrates analysed were at pH 1.5.



**FIGURE 2** Dependence of analytically determined total aluminium in filtrates of river water upon filter pore-size for Millipore and metal membrane filters. Filtrates analysed were at pH 1.5.

pore-size of membrane filter are much too large in most instances to be accounted for by analytical imprecision alone. Two separate filtrations using the same bulk water sample were performed for each pore-size, each with a new membrane filter (the average concentration from the two filtrations is given for each pore-size) and for each filtration series a concentration dependence on pore-size was evident. In addition, a filtration series using a different river water sample (Mackenzie River, near Normal Wells, NWT) was performed with Millipore membranes of different pore-size, and a concentration dependence on pore-size was evident in this case also. A series of unacidified filtrates, pH 8.3, were also analyzed, and a similar relationship of decreasing concentration of iron and aluminium in the filtrate with decreasing pore-size was found with both types of membrane filter. Data for the Arctic Red River water sample only are given here.

For Millipore type membranes the systematic change in analytical concentration occurs in the range of pore-size approximately  $0.8\ \mu\text{m}$  to  $0.25\ \mu\text{m}$ , and for metal membranes in the range of approximately  $5\ \mu\text{m}$ , to  $0.8\ \mu\text{m}$ . Analytically determined concentrations of iron and aluminium are invariably significantly higher in filtrates obtained with large-pore filters ( $5\ \mu\text{m}$ , and  $3\ \mu\text{m}$ ) than those obtained with small-pore filters ( $0.2\ \mu\text{m}$  to  $0.025\ \mu\text{m}$ ), and this is very possibly caused by a higher concentration of residual particulate matter in the former filtrates. The possibility that the observed concentration dependence on filter pore-size for iron and aluminium was caused by filter adsorption or ion exchange cannot be completely excluded, but the following speaks against such a source being the dominant cause of the concentration decrease with decreasing pore-size. All Millipore membranes used in these experiments were 142 mm in diameter while the metal membranes were only 47 mm in diameter. For a larger surface area (by a factor of 9), a reduction of ion concentration by adsorption in the filtrate was more probable for filtrates obtained with the large Millipore membranes than with metal membranes, but the opposite was found to be true in most cases, Figures 1 and 2. It was observed that the smaller metal filters were overloaded with sediment during filtration while Millipore filters were not, which may have resulted in a more complete removal of suspended particulate matter by the smaller metal filter compared to the large Millipore filter of the same nominal pore-size, with consequently lower analytically determined concentrations in the former filtrates.

When iron and aluminium concentrations are compared for filtrates acidified with hydrochloric acid and filtrates acidified with nitric acid or unacidified filtrates, Figures 3 and 4, it appears that a reduction in concentration results from hydrochloric acid in the filtrate when the concentration of these metals is relatively high (as in filtrates obtained with the  $5\ \mu\text{m}$  and  $3\ \mu\text{m}$  pore-size membranes). The possibility that the observed effect was specific

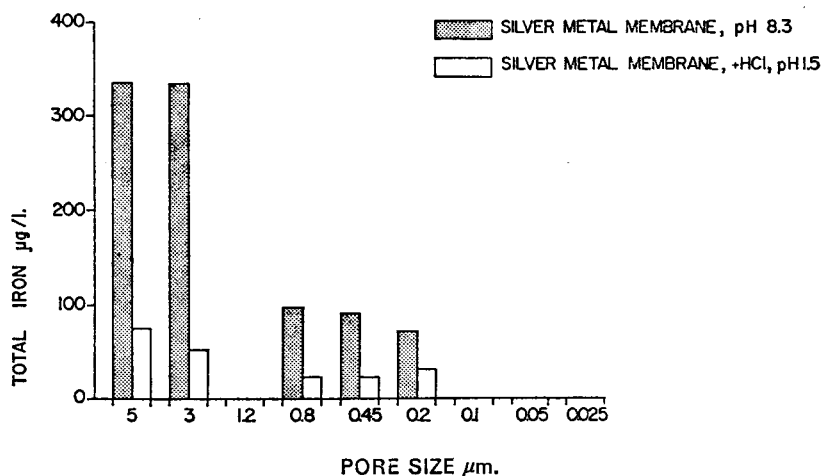


FIGURE 3 Comparison of analytically determined total iron in unacidified filtrates at pH 8.3 and in acidified filtrates, with HCl, at pH 1.5 for filtrates obtained with metal membrane filters of different pore-sizes.

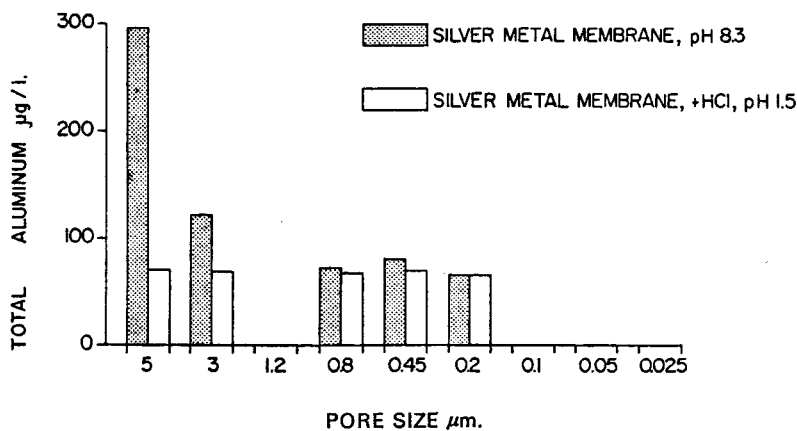


FIGURE 4 Comparison of analytically determined total aluminium in unacidified filtrates at pH 8.3 and in acidified filtrates, with HCl, at pH 1.5 for filtrates obtained with metal membrane filters of different pore-sizes.



to the method of analysis employed here for determining these metals, namely flameless atomic absorption was considered. Aluminium chloride has a relatively low temperature of sublimation, 178°C, and that of iron chloride is only somewhat higher, 300°C. Loss of these metal chlorides by sublimation during the charring segment of the analytical cycle was a possible cause of the depressing effect of hydrochloric acid on the concentrations of these elements. This explanation was not well sustained by initial result from a subsequent experiment, but this remains to be investigated more thoroughly.

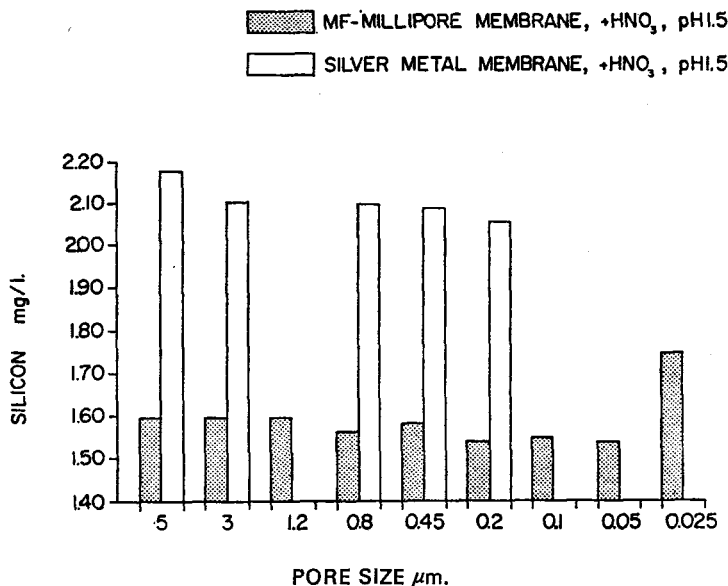


FIGURE 5 Dependence of analytically determined silicon in filtrates of river water upon filter pore-size for Millipore and metal membrane filters. Filtrates were acidified to pH 1.5 after filtration.

In contrast to iron and aluminium, silicon and magnesium concentrations are not systematically affected by a variation in filter pore-size as is evident from data in Figures 5 and 6. However, a significant difference in silicon concentration in filtrates obtained with metal membrane filters and Millipore membrane exists which clearly indicates a systematic analytical error associated with the difference in membrane materials. All silicon analyses were repeated after one month. The redetermined values differed only little from the original concentrations and passage of time and possible inconstancy of methodology were therefore not the cause of the discrepancy.

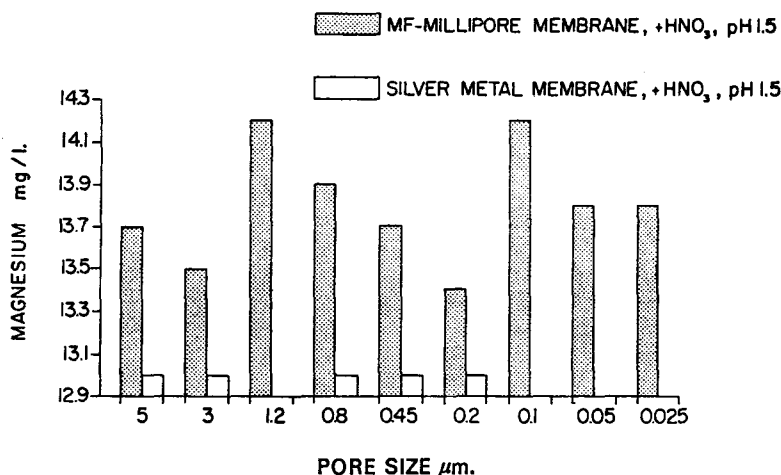


FIGURE 6 Dependence of analytically determined magnesium in filtrates of river water upon filter pore-size for Millipore and metal membrane filters. Filtrates were acidified to pH 1.5 after filtration.

It is apparent that factors other than filter pore-size, which is an important consideration to bear in mind, can cause analytical concentrations to vary considerably in applications calling for absolute rather than relative concentrations. The small difference in magnesium concentration (13.0 mg/l vs. 13.8 mg/l) in filtrates from metal and Millipore membranes is not significant.

## SUMMARY

Data presented here indicate that much of the analytically determined dissolved iron and aluminium in river water is particulate matter in the filtrate when this is obtained by filtration with Millipore filters of 0.45 μm pore-size or larger. The actual concentration of dissolved iron and aluminium is substantially lower than analytical concentrations would lead to believe. Depending on pore-size of the filter a rather wide range of analytical concentrations for iron and aluminium can be obtained in the same sample of river water. These results emphasize the importance of particulate matter in assessing the concentration of dissolved species such as iron, aluminium and possibly other trace metals. With silver metal filters of pore-size 0.8 μm and smaller, relatively uniform, low analytical concentrations of iron and aluminium were obtained and this may indicate attainment of a separation limit between dissolved and particulate matter, to a degree independent of filter pore-size. The operational definition of a dissolved substance in terms

of a 0.45  $\mu\text{m}$  pore-size silver metal membrane may therefore be less arbitrary than in terms of 0.45  $\mu\text{m}$  pore-size Millipore membrane. Analytical concentrations of silicon showed no dependence on filter pore-size, but other unknown factors not related to the chemical procedure produced discrepancies to warrant caution in using silicon concentration data on an absolute basis.

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J. E. McComiskey and G. W. Morden helped with field sampling. John Tisdale and Mike Stainton are thanked for performing some of the analyses.

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### References

1. L. H. N. Cooper, *J. Mar. Biol. Ass. U.K.* **27**, 279–313 (1948).
2. Derek W. Spencer and Peter G. Brewer, *Geochim. et Cosmochim. Acta*, **33**, 325–339 (1969).
3. W. Einsele, *Archiv. f. Hydrobiologie* **29**, 664–686 (1936).
4. W. M. Chamberlain, Ph.D. Thesis, pp. 110–113 (1968), University of Toronto.
5. F. H. Rigler, *Limnol. Oceanog.* **9**, 511–518 (1964).
6. George J. Lewis, Jr. and Edward D. Goldberg, *J. Mar. Res.* **13** (2), 183–197 (1954).
7. F. A. J. Armstrong and E. I. Butler, *J. Mar. Biol. Ass. U.K.* **42**, 253–258 (1962).
8. J. Murphy and J. P. Riley, *Anal. Chim. Acta*, **27**, 31–36 (1962).
9. F. A. J. Armstrong and S. Tibbitts, *J. Mar. Biol. Ass. U.K.* **48**, 143–152 (1968).
10. A. Henriksen, *Analyst* **95**, 601–608 (June, 1970).
11. H. Massmann, *Spectrochimica Acta*, **23B**, 215–226 (1968).
12. D. C. Manning and F. Fernandez, *Atomic Absorption Newsletter* **9**, 65–70 (1970).
13. P. E. Paus, *Atomic Absorption Newsletter*, **10**, 69–71 (1971).
14. H. C. Kahn, *American Laboratory*, pp. 35–39, (August, 1971).