the control of emissions from smaller sources. Effective abatement and control of air pollution requires that emissions resulting from the day-to-day activities of individuals and small business be significantly reduced as well as those from large industrial sources.

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References

1. Data obtained from National Air Pollution Control Administration Consultation Reports for designation of Air Quality Control Regions.
2. "Air Quality Display Model," U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration, November 1969.
3. "Air Quality Criteria for Sulfur Oxides," U.S. Department of Health, Education, and Welfare, National Air Pollution Control Administration, January 1969.
4. L. B. Lave and E. P. Seskin, *Science* **169**, 723 (1970).

6 October 1970

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Arsenic in Potable Desert Groundwater: An Analysis Problem

Abstract. *An accuracy investigation, initiated because of conflicting analytical data on the arsenic content for some 24 drinking water locations in the Mojave Desert, revealed that interference with the evolution of arsine in the American Public Health Association silver diethyldithiocarbamate method caused either color enhancement or arsine suppression. For certain types of natural waters this method is unreliable.*

Conflicting reports (*1, 2*) were published during the early part of 1969 on the arsenic content of the underground drinking water basins shown in the index map (Fig. 1). Whitnack and Brophy (*3*) had determined the As content for 15 locations at China Lake by single-sweep polarography and alleged the unreliability of the American Public Health Association colorimetric silver diethyldithiocarbamate (SDDC) method (*4*) used by most other laboratories. A comparative study of methods for the determination of As was initiated; the results of this study and the consequent investigation of metal interference in the arsine (AsH_3) evolution step are reported here. It must be recalled that the U.S. Public Health Service regards an As content of 10 parts per billion (ppb) as a caution limit and 50 ppb as a maximum allowable limit (*5*).

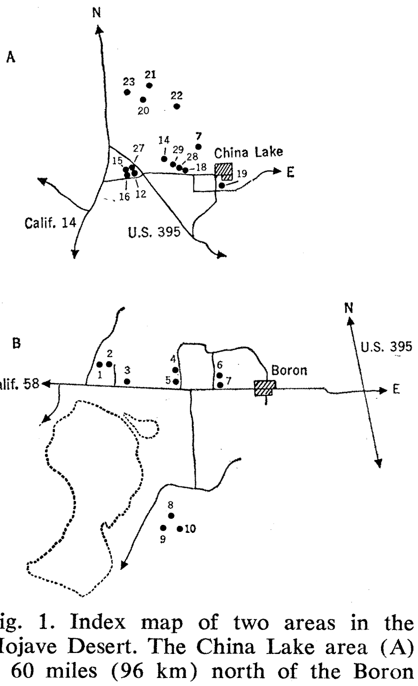

Fig. 1. Index map of two areas in the Mojave Desert. The China Lake area (A) is 60 miles (96 km) north of the Boron area (B).

The methods used for the comparative analyses on portions of 1-gallon (3.8 liters) samples of well water from the locations shown in Fig. 1 were those used by earlier investigators (*3, 4*). In addition, the x-ray fluorescence analysis of a chloroform-extracted arsenic–ammonium pyrrolidinedithiocarbamate complex of a 1000-ml aliquot was performed as reported by Marcie (*6*). One-liter portions of water samples from locations 4 and 5 were sent to a U.S. Geological Survey laboratory and a commercial laboratory, both of which used the SDDC method, in order to obtain an interlaboratory comparison. In our laboratory we analyzed water by the techniques of x-ray fluorescence and single-sweep polarography. In addition, we confirmed the reported data of the SDDC method for the Boron well locatons, using a double-beam scanning spectrophotometer (Cary model 14) and examining the absorption spectrum of the arsenic diethyldithiocarbamate color complex between 700 and 400 nm. Water samples were analyzed within 30 days.

Table 1 shows the comparison in As values derived from the three methods described. Some of the results from the SDDC method duplicate the range of values reported by up to seven laboratories over a period of 1.5 years for the Boron area. They indicate an apparent As constancy for each location of the underground water basin. In addition, Table 1 shows two significantly different As concentrations for each location. Some of the data for As derived from use of the SDDC method are larger and some of the data are smaller than the values determined by the other two methods. For example, by means of the colorimetric method no As was detected for ten locations in the China Lake area, whereas by polarography methods a range for As of 8 to 33 ppb was found for all 14 locations. Since the data derived from x-ray measurements and single-sweep polarography are in good agreement, we concluded that the SDDC data on As were suspect, especially since no increase in the polarographic As^{3+} value was obtained when samples were treated with hydrazine to reduce any As^{5+} present. Loss of As or AsH_3 inhibition was assumed to have occurred in those cases where the SDDC values were lower. All colorimetric analyses were reproducible within the preci-

Table 1. Comparative data on the amount of arsenic (in parts per billion) at two sites in the Mojave Desert; N.D., not detected (<2 ppb); N.A., not analyzed.

Location of sample (Fig. 1)	Methods of analysis		
	SDDC	Single-sweep polarography	X-ray fluorescence
		*China Lake**	
7	N.D.	19	N.A.
12	N.D.	27	N.A.
14	N.D.	8	N.A.
15	N.D.	27	N.A.
16	N.D.	27	N.A.
18	6	25	N.A.
19	8	19	N.A.
20	N.D.	8	N.A.
21	N.D.	16	N.A.
22	N.D.	33	N.A.
23	N.D.	19	N.A.
27	29	16	N.A.
28	N.D.	27	N.A.
29	22	27	N.A.
		Boron	
1	110–250	N.A.	N.A.
2	110–250	15	N.A.
Faucet at 1	160	8	5
3	330–400	13	15
4	70–80	25	N.A.
5	50	25	N.A.
Faucet at 5	28–50	18	10
6	90	N.A.	15
7	45	N.A.	N.A.
Faucet at 6, 7	50	10	10
8	N.D.	11	8
9	30	8	5
10	N.D.	8	8

* See (*3*).

Table 2. Interference in the arsine evolution step due to added CrO_4^{2-} and MoO_4^{2-}. An absorbance of 0.40 is obtained for a 10-μg As standard solution when the light beam (525 nm) of the spectrophotometer passes through the colored solution (cell thickness, 1 cm). On the basis of an equal absorbance for a 50-ml water sample, the concentration of As is calculated to be 200 ppb. N.A., not analyzed; N.D., not detected (< 2 ppb).

Location of sample (Fig. 1)	Sample as received (ppb)	Arsenic calculated (ppb) in the presence of		
		CrO_4^{2-} added (ppb)		MoO_4^{2-} added (ppb)
		16	32	56
1,2 composite	110	170	160	8
3 composite	330	340	N.A.	250
4,5 composite	19	45	30	7
6,7 composite	50	N.A.	50	48
8	N.D.	2	N.A.	N.A.
9	30	20	N.A.	N.A.
10	N.D.	1	N.A.	N.A.
8,9,10 composite	30	N.A.	N.A.	N.D.
10-μg As standard				
	200	215	195	160

sion reported (*4*), and standards were checked and cross-checked.

A review of the recent literature (*7*) plus several experiments with a polycarbonate arsine generator revealed that several metals interfere with the evolution of AsH_3. An analysis of the underground water basins at China Lake and Boron was initiated to determine the trace element constituents for well locations of interest, especially since in the x-ray fluorescence analysis the presence of interfering metals had been detected. The following metals were determined by flame emission and atomic absorption spectroscopy, single-sweep polarography, and x-ray fluorescence analysis: Ag, Li, Sr, Cu, Pb, Ni, Zn, Co, Mn, Au, Sb, Al, V, Mo, Cr, and Fe. The content of trace metals at all locations ranged from 2 to 500 ppb for each element. The amounts of the trace element constituents varied from location to location but there is an indication of a broad compositional similarity for the two water basins. A problem of greater importance to the study of AsH_3 evolution and color interference was the determination of the in situ molecular species of Cr, Mo, V, and other elements that may occur in the alkaline (*p*H 8) drinking water. These species have been identified by polarography as chromate, metavanadate, molybdate, and iodate, and their concentrations in the water samples ranged from 2 to 200 ppb. The quantity of each anion varied from location to location but all four anions were found at each location listed in Table 1. In addition, nitrate and fluoride ions are present at concentrations of several parts per million (ppm). The F^- ion has a range of 0.5 to 3.0 ppm, and its role in AsH_3 interference has not been investigated.

Interference caused in the evolution of AsH_3 was observed when parts-per-billion quantities of chromate or molybdate ions were added to 50-ml water samples from several locations. [A polycarbonate generator was used because Pyrex glassware reportedly (*8*) contains some of the same trace impurities as those that were to be added.] Results obtained for pooled samples from locations 1 and 2 and from locations 3 and 4 illustrate a chromogenic enhancement effect and an AsH_3 suppression effect for the same locations with molybdate (Table 2). It is apparent that many competing and complex reactions occur in the highly reducing ($SnCl_2$) and acidic (1*M* HCl) environment of the AsH_3 evolution step of the SDDC method. For example, a marked reduction in the amount of hydrogen gas evolved was observed with each sample to which 56 ppb of molybdate had been added. A slower rate of hydrogen evolution was also noticed with untreated samples from locations 8 and 10, which contain significant amounts of metavanadate ions. It is known that molybdenum and vanadium arsenite complexes may form under the conditions existing in the AsH_3 generator, and formation of either of these complexes would suppress the evolution of AsH_3. No general explanation can yet be given for the color enhancement effect, although it is probable that other chromogens (metals chelated to diethyldithiocarbamate) are formed in the AsH_3 absorber with mineralized water samples, as illustrated in Fig. 2. A standard solution of As does not exhibit color enhancement after the addition of parts-per-billion quantities of chromate. Color enhancement may cause an elevation of the base line for arsenic diethyldithiocarbamate at 525 nm, and this elevation would lead to an inaccurately high As content for a given sample. Reproducibility and high precision are assured as long as the concentration of the interfering constituent remains constant. The absorbance peak at 410 nm may be due to the chromium diethyldithiocarbamate complex, although it is not known by what mechanism Cr can be carried from the AsH_3 generator to the absorber which contains the SDDC-pyridine solution.

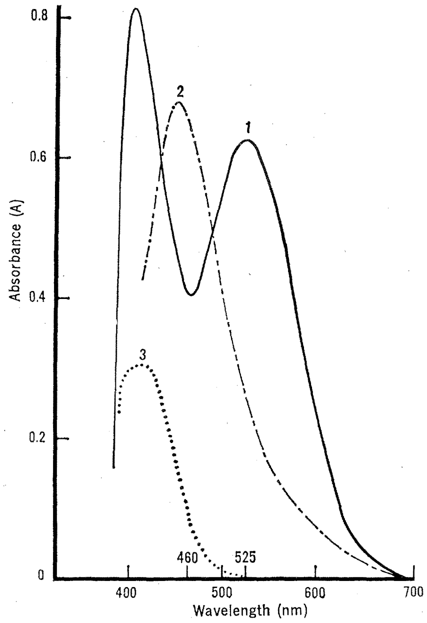

Fig. 2. Absorbance spectrum of the arsenic diethyldithiocarbamate chromogen, illustrating the enhancement effect due to an elevated base line at 525 nm with the SDDC test procedure. A double-beam scanning spectrophotometer (Cary model 14) was used; 1-cm cells were used in both reference and sample beams. Curve 1, arsenic diethyldithiocarbamate absorption spectrum for location 3 (Fig. 1B); curve 2, copper diethyldithiocarbamate absorption spectrum; curve 3, chromium diethyldithiocarbamate absorption spectrum.

It is known, however, that SDDC will chelate with many metals, some of which have absorbance maxima between 450 and 550 nm; the absorbances of these chelates would thus interfere with or be coincident with the absorbance of the arsenic diethyldithiocarbamate chromogen at 525 nm. The molar absorptivity of the copper diethyldithiocarbamate and chromium diethyldithiocarbamate chromogens is estimated to be several orders of magnitude larger than that of the arsenic diethyldithiocarbamate color complex, according to preliminary data obtained by us.

It is probable that the inability to detect As by means of the SDDC method (Table 1, column 2, entries marked

N.D.) for ten locations at China Lake and for two locations at Boron are a direct result of interference due to VO_3^- and other anionic metal complexes. It also is significant that the data on As content from single-sweep polarography are in good agreement with the SDDC data only for a single well location, namely, location 29 of Table 1. In view of the projected importance of water pollution analysis, several conclusions have been derived from the work reported:

1) The underground waters of the Boron and China Lake basins are associated with heterogeneous rock formations, many of which contain large amounts of water-soluble minerals. Thus, the subsurface water more closely resembles dilute brines or even brackish seawater (*1*) than it does the usual surface waters for which the colorimetric SDDC method was developed. In the SDDC test procedure (*4*) the analyst is cautioned (paragraph 1.2) about interference with AsH_3 evolution caused by certain metals; all the metals listed in paragraph 1.2 were found in our mineralized water samples. Stratton and Whitehead (*9*) and Ballinger *et al.* (*10*) developed and evaluated the SDDC method for relatively pure river drinking water, and neither of these groups of authors found it necessary to use a second method of known accuracy and specificity for As to verify their results.

2) It is recommended that the SDDC method be used for the routine analysis of desert water only after verification of the As content by means of x-ray or single-sweep polarographic measurements. Angino *et al.* (*11*) cited the presence of the same interfering metals in detergents as those reported here but they evidently ignored the caution in paragraph 1.2 of the SDDC test procedure in their statement that a high degree of precision in the determination of As was attained. No mention was made of the degree of accuracy obtained.

3) Accurate and highly specific analytical methods should be employed by concerned agencies to correctly detect the presence of and to define the extent of water pollution. The accurate analysis of trace toxicants in water in the parts-per-billion range is difficult, at best, and research efforts in this area are vitally needed, as advocated by Smith (*12*).

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References

1. State of California, 6th Regional Water Quality Control Board, Bishop, Calif., "Report on Arsenic Occurrence in the North Muroc Hydrologic Basin" (Feb. 1969).
2. *Naval Weapons Center, China Lake, Calif., Tech. Mem.*, "The Determination of Arsenic in Drinking Water" (March 1969).
3. G. C. Whitnack and R. G. Brophy, *Anal. Chim. Acta* **48**, 123 (1969).
4. *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association, New York, ed. 12, 1965), p. 56.
5. *Federal Register*, Title 42, Public Health Service, Part 72 (6 March 1966).
6. F. Marcie, *Environ. Sci. Technol.* **1**, 165 (1967).
7. E. B. Sandell, *Colorimetric Determination of Traces of Metals* (Interscience, New York, ed. 3, 1959); O. Menis and T. C. Rains, *Anal. Chem.* **41**, 952 (1969); K. E. Burke and M. M. Yanak, *ibid.*, p. 963; A. Arnold *et al.*, *Analyst* **94**, 664 (1969).
8. D. E. Robertson, *Anal. Chem.* **40**, 1067 (1968).
9. G. Stratton and H. C. Whitehead, *J. Amer. Water Works Ass.* **54**, 861 (1962).
10. D. G. Ballinger, R. J. Lishka, M. E. Gales, Jr., *ibid.*, p. 1424.
11. E. E. Angino, L. M. Magnuson, T. C. Waugh, O. K. Galle, J. Bredfeldt, *Science* **168**, 389 (1970).
12. R. G. Smith, *Anal. Chem.* **40**, No. 7, 24A (1968).

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Paradox of Enrichment: Destabilization of Exploitation Ecosystems in Ecological Time

Abstract. *Six reasonable models of trophic exploitation in a two-species ecosystem whose exploiters compete only by depleting each other's resource supply are presented. In each case, increasing the supply of limiting nutrients or energy tends to destroy the steady state. Thus man must be very careful in attempting to enrich an ecosystem in order to increase its food yield. There is a real chance that such activity may result in decimation of the food species that are wanted in greater abundance.*

Schemes for increasing primary productivity by enriching an ecosystem's energy or nutrient flow are much in evidence today and are probably a reflection of the increasing demands of the world's population. Such schemes may end in catastrophe.

In 1963, Huffaker, Shea, and Herman (*1*) reported destabilization of a stable exploitation ecosystem which resulted in the extinction of both the exploiter (an acarophagous mite) and its victim (an herbivorous mite). They produced this result by trebling the herbivore's food density. By using a variety of realistic models, I predict that instability should often be the result of nutritional enrichment in two-species interactions.

Rosenzweig and MacArthur (*2*) showed that exploitation (or predator-prey) ecosystems do not necessarily exhibit any oscillations. Furthermore, even if there are oscillations, they do not last under ordinary circumstances. If the exploiter is quite proficient at reproducing in the presence of few of its victims, then the ecosystem does not persist. If, however, the victims are relatively proficient at escape or their exploiters have a relatively poor reproductive efficiency or digestive efficiency, then the system will persist in ecological time (*3*).

The dividing line between persistent and explosive systems is definable from a general graph of exploitation (*2*). The victim's density V is plotted against P, the exploiter's density. The collection of graph points at which $dV/dt = 0$ is called the victim's isocline. The collection of points at which $dP/dt = 0$ is called the exploiter's isocline. Any point of intersection between the two isoclines is an ecosystem equilibrium, but not all such equilibria will result in a steady state. The usual form of the prey isocline is a hump (*4*). If the equilibrium is at a point on the left side of the hump, the predator is too proficient and the system will ordinarily not persist. If equilibrium is at a point on the right-hand (downslope) side of the hump, the system will persist. Thus, the hump's peak is over a critical value of V, V^*. If the equilibrium value of V is larger than V^*, the system is safe. If not, it is in danger of extinction.

If the exploiters do not actually interfere with each other directly—if they never battle over the same individual victim or engage in cannibalism or territorial defense—then the P isocline is a simple vertical line ($V = J$). The position of this line is fully determined by the phenotypes of the exploiter and its victim. It does not change with nutrient flow or energy supply.

To discover the effect of enriching a system, one needs to find how V^* changes as enrichment proceeds. If enrichment increases V^*, then it is jeopardizing the system, because eventu-