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CONTACT REPORT

Via Telephone - February 25, 1959

People in Conference:

M. R. Barusch, California Research Corporation
M. E. Griffing, Ethyl Corporation

Subject: Determination of Tetramethyllead in Air

This call was made at the suggestion of Mr. Gibson as a result of his conversation with Mr. J. L. Cooley and Mr. J. R. MacGregor on February 10. The purpose of the call was to discuss the details of the analytical procedure and to reconcile any differences in experience between the two Laboratories. Since quantitative recovery may have been obtained in part of their experiments and not in others, this call was not made until sufficient new data had been collected to define the conditions under which correct TML analyses could be obtained. Prior to calling Dr. Barusch, a telephone call was made to Dr. Hudson and Mr. Johnson of our Baton Rouge Laboratories so that our report could represent the combined opinion of both groups. The following subjects were discussed: 1) Qualification of the low recovery data phoned by Mr. Gibson; 2) Speed of reaction of iodine with TML and TEL; 3) Review of the efficiency of the lead-in-air kit for TEL; 4) Efficiency of the scrubbers for TML; and 5) Specific recommendations for making safe determinations of TML in air. The conversation is summarized below along with the actual data used as a basis for the conclusions and recommendations.

Dr. Barusch was happy to receive this information and felt that it would be adequate as a basis for evaluating their own data. Hw was relieved to learn that the previously phoned recovery data for TML were not applicable to the conditions used in his work and felt that their data were grossly correct. I pointed out to him that the work done by Mr. Hirschler on the relative volatilities of TML and TEL had been done at a flow rate of 0.1 cu ft per minute and were also grossly correct.

Dr. Barusch said that they were amazed that the method was as good as it was and that their only difficulty had involved the formation of a brown solid when sampling from a highly olefinic fuel. They removed this by rapid filtration before developing the color. I told him we had had similar experience through the years and had removed these colored materials by extraction with chloroform just before extraction with the chloroform solution of dithizone.

Dr. Barusch had no suggestion for additional work and agreed that the field kit should be safe for monitoring the air in areas where fuels containing TML were to be handled or blended. I re-emphasized the need for slower than usual flow rates and two scrubbers in series to assure the efficiency of sample collection. I told him that the Detroit Laboratories planned no

additional work but that the Baton Rouge Laboratories would continue to work on a more efficient scrubber.

1. Previously Phoned Recovery Data - These data, which reported that only 24 per cent recovery of TML had been achieved at a flow rate of 0.12 cu ft per minute, where not obtained with the iodine solution recommended in the lead-in-air kit. They were obtained with a solution containing a higher concentration of potassium iodide, which decreased the vapor pressure of iodine over the solution. Our experience has indicated that some of the reaction takes place in the vapor phase and much of it on the glass wool. Therefore it is reasonable that increased potassium iodide would decrease the efficiency of the scrubber. (TWX R. L. Hudson to S. O. Rue on February 9 and Memorandum RLH to SOR on February 13, "TML in Air Determination".)

2. Relative Reaction Rates of TML and TEL - We have experienced the same slowness in the reaction of TEL to form lead ion which was reported to Mr. Gibson by California Research Corporation, but we had expected the rate for TML to be even slower. We had concluded that the low recovery of TML might be explained by slowness of this reaction. To check this point we added known quantities of TML and TEL to aliquots of the iodine solution, quenched the iodine after measured periods of time, carried out the kit reactions, observed the hue of the dithizone solution, and measured its intensity. We concluded that the complete conversion of TML to lead ion was achieved in a shorter time than the conversion of TEL to lead ion. The data are shown on Table 1.

We pointed out that even though the overall rate of reaction of TML was faster than that for TEL, the reaction time was finite and large in comparison to the residence time in the scrubbers. Therefore scrubbers in series were essential to assure good analyses. (TWX from D. E. Johnson to S. O. Rue, February 25, 1959 was received after our phone call. They studied the reaction of iodine with both TEL and TML to form the trialkyllead salts and found that TEL formed this salt more rapidly than TML. The further reaction of trimethyllead iodide to lead ion was more rapid than the reaction of triethyllead iodide. Therefore the findings of the two laboratories are consistent and support the recommendations of two scrubbers and slow flow rates.)

3. Efficiency of the Lead-in-Air Kit from TEL - To make sure that the scrubbers were packed properly with the glass wool and that the solutions were satisfactory for the determination of TEL in air, a series of gas samples containing TEL was prepared and analyzed by the field kit method. Three scrubbers were used in series and each solution was analyzed separately. Samples contained from 4 to 6 micrograms Pb per cu ft. The results showed that from 90 to 100 per cent of the lead was collected in the first scrubber. The data are shown in Table 2. The uncertainty of the method makes it questionable that any of the TEL was found in the second scrubber.

4. Efficiency of the Lead-in-Air Kit for TML - Our experience has shown that all variables are more critical for the determination of TML than for the determination of TEL. Our Baton Rouge Laboratories have found some difficulty in preparing two scrubbers to give the same efficiency in collecting TML vapors. There is loss if only one scrubber is used and especially at high flow rates.

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We prepared TML vapor samples as follows: A gasoline was blended to contain approximately 3 g of Pb as TML in one gallon. Air samples of varying concentrations were prepared by drawing air from various heights above the surface of a fresh sample of the gasoline. The sample was drawn through three scrubbers in series, which had been efficient for TEL in air analyses. The solution in each scrubber was analyzed separately and the total lead in the air was calculated from the sum. If only a trace of lead was found in the third scrubber, it was assumed that the correct concentration of lead in vapor could be calculated from the total lead and the measured volume. The results are shown in Table 3.

The following conclusions were passed on to Dr. Barusch:

a. For concentrations of 20 to 200 micrograms of Pb per cu ft and with a flow rate of 0.1 cu ft per minute, 75 to 80 per cent of the lead is collected in the first scrubber and 95 to 100 per cent is collected in the first two scrubbers.

b. For concentrations of 8 to 25 micrograms of Pb per cu ft and a flow rate of 0.3 cu ft per minute, 50 per cent of the lead is collected in the first scrubber and 85 to 95 per cent in the first two scrubbers.

c. For concentrations of 8 to 20 micrograms of Pb per cu ft and with a flow rate of 0.5 cu ft per minute, 42 to 50 per cent of the lead is collected in the first scrubber and 85 per cent of the lead is collected in the first two scrubbers.

5. Specific Recommendations for Determining TML in Air - Variability among scrubbers, the importance of the glass wool packing, and the effect of iodine concentration and the flow rate on the recovery of TML suggested the following precautions which were emphasized as specific recommendations to Dr. Barusch:

a. Use the scrubbers and solution recommended in the lead-in-air kit.

b. Use two scrubbers in series and analyze their solutions separately. Consider any analysis suspect if the second scrubber contains more lead than the first.

c. Use a fine glass wool, make sure that adequate packing is used and that channelling does not occur.

d. Use a flow rate of 0.3 cu ft per minute for low concentrations of TML and of 0.1 cu ft or less for high concentrations of TML.

If these conditions are observed we believe that the present lead-in-air kit will provide a convenient and safe method for monitoring the lead in air in areas where gasoline containing TML is blended or handled.

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Table 1 - RATES OF REACTION OF TEL AND TML WITH IODINE

Lead Compound	Pb in µg	Time of reaction in min.	Per cent reacted *
TEL	28	1	40
		2	60
		5	100
TML	30	1	75
		2	100
		5	100

* Based on formation of Pb^{++}, which is measured by the lead-in-air kit.

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Table 2 - RECOVERY OF TEL FROM AIR

TEL concentration µg Pb/cu ft *	Sample volume, cu ft	Flow rate, cu ft/min	Per cent recovered in 1st scrubber
4	4	0.1	100
4.5	2	0.3	89
3.5	4	0.3	86
6.1	4	0.5	92

* Calculated from total lead recovered and measured volume; in each case the third scrubber was free of lead.

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Table 3 - RECOVERY OF TML FROM AIR

Flow rate, cu ft/min	TML concentration µg Pb/cu ft *	Sample volume cu ft	Per cent recovered 1st Scrubber	2nd Scrubber
0.1	196	0.5	74	26
	62	1	94	6
	47	1	68	32
	52	2	80	20
	43	3	77	21
	20	4	73	23
0.3	23	2	52	43
	8	4	53	34
0.5	20	2.5	50	35
	8	4	42	42

*Calculate from total lead recovered and the measured gas volume. In each case the third scrubber contained no lead or only a trace.