

A STUDY OF DERMAL AND INHALATION EXPOSURE
OF MIXER-LOADERS AND APPLICATORS
TO NITROFEN IN MONTEREY AND SANTA BARBARA
COUNTIES OF CALIFORNIA

by

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SUMMARY

Potential inhalation and dermal exposure of mixer/loaders and applicators to nitrofen (TOK) or 2,4-dichloro-1-(4'-nitrophenoxy)-benzene, CAS 1836-75-5, was measured in the Salinas and Santa Maria Valleys of California during May, June, and July, 1980. Worker exposure was measured during the 2 major phases of ground-spray application, the mixing and loading operation and the actual spraying, with both TOK E-25 (emulsifiable concentrate) and TOK WP-50 (wettable powder). The study involved 14 loading operations (7 with TOK E-25, 5 with TOK WP-50, and 2 with TOK WP-50 packaged in water-soluble bags), and 9 timed-spraying trials (4 with TOK E-25 and 5 with TOK WP-50). Inhalation exposure was measured by sampling the air inside and outside the respirator during the mixing, loading, and application operations. Dermal exposure while mixing, loading, and applying TOK was measured utilizing cloth pads placed over the thigh, chest, sleeve, and back portions of the worker's coveralls, and by collecting handwashes following each separate operation.

During the mixing/loading operation of TOK E-25 and TOK WP-50, air was monitored inside and outside the respirator for 11- to 27-minute working periods. Inhalation levels inside the respirator ranged from below the minimum detectable level to 28 $\mu\text{g}/\text{m}^3$ using TOK E-25, with an average of 8 $\mu\text{g}/\text{m}^3$; from 18 to 294 $\mu\text{g}/\text{m}^3$ using TOK WP-50 in bulk, with an average of 99 $\mu\text{g}/\text{m}^3$; and from below the minimum detectable level to 20 $\mu\text{g}/\text{m}^3$ using TOK WP-50 in water-soluble bags, with an average of 10 $\mu\text{g}/\text{m}^3$. Levels outside the respirator ranged from below the minimum detectable level to 599 $\mu\text{g}/\text{m}^3$ using TOK E-25, with an average of 86 $\mu\text{g}/\text{m}^3$; from 4301 to 22606 $\mu\text{g}/\text{m}^3$ using TOK WP-50, with an average of 13714 $\mu\text{g}/\text{m}^3$; and from 89 to 163 $\mu\text{g}/\text{m}^3$ using TOK WP-50 in water-soluble bags, with an average of 126 $\mu\text{g}/\text{m}^3$.

During the application of TOK E-25 and TOK WP-50, air was monitored in the same manner for time intervals ranging from 31- to 115-minute working periods. Inhalation levels inside the respirator ranged from below the minimum detectable level to 10 $\mu\text{g}/\text{m}^3$ using TOK E-25 with the only measurable level being 10 $\mu\text{g}/\text{m}^3$; and, using TOK WP-50, ranged from below the

TOK WP-50 is packaged in 5 pound paper bags; 8 of these bags (40 lbs.) are contained in a larger sack, which is the unit the product is sold in. TOK E-25 is sold in 5 and 30 gallon metal cans. The manufacturer states that they propose to package the wettable powder formulation in water-soluble bags; this method of packaging has been shown to substantially reduce mixer/loader exposure to powders as compared with those packaged in bulk.

With proper handling, in accordance with label instructions, TOK has not been considered a hazardous product capable of causing significant acute illness. The few acute illnesses that have occurred in California related to spills on the skin or inhalation of significant amounts of the chemical in the aerosol form. Serious illness could be expected to follow accidental or intentional ingestion of TOK. No long-term illnesses, illnesses with delayed onset, or deaths, are known to have occurred from exposure to this chemical. No cases of human cancer or damage to human embryos have been documented.

Recent animal studies by Ambrose et al. (1971) and Kimbrough et al. (1974) have shown TOK to be a potent teratogen. Other animal studies by Paik and Lee (1977), Milman et al. (1978) and the National Cancer Institute (1978) have shown TOK to be a possible mutagen and carcinogen.

The potential for teratogenicity (damage to the fetus in a pregnant female) is the most serious concern. The primary defect is failure of the lung to function properly at birth.

This product is now considered to be difficult to work with safely because recent animal studies reported by Burke (1980) have shown that TOK, as formulated, has dermal absorption rates of 60-95 percent within 24 hours of application to animal skin.

There is a new general concensus that women who know they have a potential of becoming pregnant should avoid exposure to this chemical. Damage might occur to the embryo even before the woman knows she is pregnant, since the damage is assumed to occur in the first 3 months of pregnancy.

Upon learning of the animal studies showing a rapid and high absorption rate, the California Department of Food and Agriculture further examined the developing information on chronic health effects in test animals.

In May 1980, the California Department of Food and Agriculture adopted emergency regulations concerning the use of TOK. These regulations classified TOK as a restricted material requiring a permit from the county agricultural commissioner for its possession and use, and imposed the following additional use restrictions:

1. Females shall not mix, load, or apply TOK.
2. Applicators must wear long-sleeved shirts and long pants, a waterproof hat, rubber or neoprene gloves and boots, eye protection, and a respirator during application. All the above plus an apron are required for persons mixing and loading TOK.

Inhalation exposure during the mixing and loading operation was monitored by plumbing a sampling tube in to the respirator and drawing air through a collection tube with a Mine Safety Appliance Model "g" pump. Another air sample was taken outside of the respirator to determine respirator efficiency. Duplicate sampling tubes were used during the actual application. The collection medium used is a 6 x 70 mm glass tube containing 120 mg XAD4 resin. (SKC-West, Inc., catalog number 226-30-11-04.) The tubes were capped and chilled on ice when sampling was complete.

Dermal exposure was measured by using sampling pads, strategically attached to coveralls by the method of Durham and Wolfe (1962) and Wolfe (1967); and by collecting handwash samples following each separate operation. Pads were constructed in the following sequence, from inner to outer layer: (1) 1 sheet of paper, (2) 1 sheet of aluminum foil, (3) a layer of 8 pieces of gauze, and (4) a layer of 6-ounce cotton duck cloth. The cloth and gauze were preextracted with acetone to remove contaminants. The pads measured 4 inches square and were held together by taping the perimeter with masking tape. Sampling pads were placed on the thighs, on both sides of the upper chest near the collar, and on each forearm; and 1 pad was placed on the back just below the collar. They were pinned to 2 pairs of disposable coveralls. One pair was worn by the employee while mixing and loading, and the other pair was worn during the actual spraying.

Following the application, the coveralls were carefully removed, and the pads were taken off the coveralls. The pads were then cut to remove the masking tape edge, using a 7.5 cm square template. (The final surface area of each pad is 56.25 cm².) The layers of each sampling pad were separated as follows and placed in glass jars: (1) the cotton duck cloth, and (2) the gauze and foil. The paper backing was discarded. Matched pairs of the thigh, chest, and forearm patches were combined. (For example, both left and right mix-load/thigh/duck cloth layers were combined as were both left and right application/chest/gauze-foil layers.)

Previous studies by Peoples et al. (1979) and Davies (1979) have shown the hands to be a primary route of exposure to airborne pesticides. Handwash samples were collected to measure total hand exposure to TOK.

At the end of each loading and each application, a handwash sample was collected in the following manner: A 250 ml separatory funnel was filled with deionized water and held on a ringstand over a stainless steel bowl. The worker held his hands under the funnel and a small amount (approximately 10 ml) of water was run over his hands. A drop of Ivory Liquid detergent was placed on the hands and lathered well, covering all surfaces. The remainder of the water was then released from the funnel over the hands as rubbing continued. The wash water was then poured into a 16 ounce jar. The hands were washed in the same manner prior to each study period. After each study period, the hands were rinsed with 95% ethyl alcohol, and the alcohol was retained as a sample.

The large majority of TOK applications in California are made by licensed pest control operators using standard-sized row-crop tractors that apply a band spray on the soil where the plants will be or have been planted. This is the application method that was studied.

day's exposure. This was estimated to be 1 hour total time mixing and loading TOK and 4 hours applying TOK. Column D is an estimate of the average area of the skin of each body part in square centimeters, according to Berkow (1931) and DuBois (1916). This assumes an average man, weighing 70 kg and standing 175 cm. Column E is an estimate of the dermal exposure to TOK in micrograms per day to each body part. The calculations for the anterior portion of the head and neck use a combination of TOK residues on the outside cloth and inside gauze samples taken on the upper chest to represent exposure of bare skin to airborne TOK. (This assumes no face protection from respirator or shield.) Calculations for the posterior portion of the head and neck use a combination of the TOK residues on the outside cloth and inside gauze sample taken on the upper back, just below the neck. Calculations for the anterior portion of the trunk use the gauze portion of the sample taken on the upper chest to simulate skin covered with clothing. Similarly, calculations for the posterior portion of the trunk use the gauze portion of the sample taken on the upper back; the arms and forearms use the gauze portions of the sample taken on the forearms; and the thighs, legs and feet use the results from the gauze portion of the sample taken on the front of the thigh, just above the knee. Column F is the sum of the exposure to the body parts, excluding the hands, and inhalation exposure.

Table 3 - The dermal exposure of worker's hands using handwash sampling.

Column A is an estimate of the total daily exposure for each work activity. This assumes a typical maximum work day of 1 hour mixing and loading, and 4 hours applying. Column B is the sum of these 2 exposure levels.

Note: The method used for gathering these samples, described in the "Materials and Methods" section was found to be only partially effective in removing nitrofen from the hands. Data indicate that detergent and water washes gathered approximately 85 percent of the TOK WP-50 and 67 percent of the TOK E-25 from the hands. The remainder was gathered by an alcohol rinse at the end of the study period. Gloves worn by the employee may be contaminated from earlier exposures to TOK. Preliminary data indicates that an average of 2000 ug of TOK accumulates in the gloves. Transfer of this material to the skin of the hands would presumably elevate exposure levels. It should be noted however that this is only an approximation. Further studies are needed to determine the best method to monitor hand exposure to pesticides.

Table 4 - Total of dermal and inhalation exposure during a full day's work with TOK. Column A is the total exposure monitored, from Column F of Table 2. Column B is the total exposure monitored, from Column B of Table 3. Column C is the total exposure monitored from Columns C and D of Table 1. Column D is calculations of estimated total body exposure for a typical maximum work day. It is estimated that the usual maximum time an employee would work with TOK is 1 hour per day mixing and loading, and 4 hours per day applying. Estimates are made assuming both use and no use of a half-face respirator.

During the application of TOK E-25 and TOK WP-50, air was monitored in the same manner for time intervals ranging from 31- to 115-minute working periods. Inhalation levels inside the respirator ranged from below the minimum detectable level to 10 ug/m^3 using TOK E-25, with the only measurable level being 10 ug/m^3 ; and, using TOK WP-50, ranged from below the minimum detectable level to 94 ug/m^3 , with an average of 44 ug/m^3 . Measurements outside the respirator for applying TOK E-25 ranged from below the minimum detectable level to 17 ug/m^3 , with an average of 14 for the detected levels; for TOK WP-50 the values ranged from 31 to 385, with an average of 102 ug/m^3 .

Handwashes and sampling pads were used to estimate the amount of TOK which contacted the skin. The total amount of TOK (in micrograms) estimated to reach a person's skin during a series of mixing/loading operations totaling 60 minutes ranged from 185 to 2317 when using TOK E-25, with an average of 783; from 3048 to 5648 when using TOK WP-50 in bulk, with an average of 4341; and from 5681 to 21344 when using TOK WP-50 in water-soluble bags, with an average of 13518.

The total amount of TOK (in micrograms) estimated to reach a person's skin during a full day's application operations (4 hours) ranged from 431 to 4097 when using TOK E-25, with an average of 2068; and from 1193 to 3839, with an average of 2547 when using TOK WP-50.

A survey of use patterns in California indicates that the typical maximum daily exposure to TOK for a mixer/loader/applicator of pesticides would involve 1 hour of mixing/loading, and 4 hours of application of TOK. For these applicators using TOK WP-50 in bulk, their daily exposure would be 7230 ug; when using TOK E-25, it would be 3003 ug; and when using TOK WP-50 packaged in water-soluble bags, it would be 15992 ug. Using the no-observed-effect level for teratogenicity of 300 ug/kg of body weight per day, and assuming an average body weight of 70 kg, the safety factor provided by each product is: 2.9 for TOK WP-50 in bulk, 7.0 for TOK E-25, and 1.3 for TOK WP-50 in water-soluble bags. This assumes that a hat, coveralls, respirator, gloves, and boots are used for all phases of TOK mixing, loading, and application.

One additional trial of TOK E-25 was conducted (at a site where TOK WP-50 had not been used) in which sampling for mixing/loading and applying was combined. This was a 105-minute trial during which 2 loads of TOK E-25 were mixed, loaded, and sprayed. The concentration of TOK outside the employee's respirator was 20 ug/m^3 . The total amount of TOK estimated to reach the employee's skin--excluding his hands--during a full work day, was 4269 ug. Daily hand exposure was estimated at 106 ug. Total daily (4 hour) body exposure was estimated at 4500 ug without the use of a respirator.

The exposure when using TOK WP-50 packaged in water-soluble packets was far greater than expected from previous observations on use of water-soluble packets. These poor results were attributed to an incident which occurred during the study. During the shipment of the product in water-soluble packets from the manufacturer to the field, at least 1 of the water-soluble packets burst open. The loader's hands were heavily contaminated when opening the paper bag containing the burst packet. Previous experience

2. The use of closed-system mixing and loading (with built-in probes) of the emulsifiable concentrate dramatically reduces exposure as compared to the open-pouring procedures studied by Rohm and Haas.
3. The safety factor provided by use practices and regulations in effect during the study period still were not sufficient to allow women capable of becoming pregnant to mix, load or apply TOK to protect the fetus from the potential teratogenic effects of TOK.
4. Without additional safe handling techniques and/or safety equipment being put into effect, it appears that an insufficient safety factor is provided men and women who mix, load, or apply to protect them from TOK's potential mutagenic and carcinogenic effects.
5. Although the use of water-soluble packaging of wettable powders has the potential to substantially reduce the exposure of the mixer/loader, the trial exposure conducted of this use was not satisfactory because the bags, when shipped from the manufacturer, were not adequately packed. At least 1 packet was found already broken when the outer bag was opened, which resulted in excessive exposure of the mixer-loader.
6. Further, reduction in exposure level could be obtained by reducing the mixer/loader's exposure to the wettable powder formulation and/or reducing the applicator's exposure to spray drift from either formulation. The latter may be accomplished by outfitting the tractor driver in waterproof clothing or providing protection with a closed cab tractor with an air filtration system. Additional protection to the mixer/loader could be provided by requiring that disposable gloves be used and discarded twice daily. Work rules (regulations) could prohibit opening the mix tank for any reason once a toxicity category one liquid has been pumped in.

TABLE 2

Concentration of TOK Found in the Respirator and Breathing Zone (Ambient) of Employees While Mixing, Loading, and Applying TOK in Monterey and Santa Barbara Counties of California

Plot Number	Type of Formulation	Column A		Column B		Column C		Column D
		Concentration of TOK While Mixing and Loading (ug/m ³)	Concentration of TOK While Applying (ug/m ³)	Total Estimated TOK Inhalation Exposure Per Day When Wearing Respirator (micrograms)	Total Estimated TOK Inhalation Exposure Per Day Without the Use of a Respirator (micrograms)			
		Inside Respirator	Ambient	Inside Respirator	Ambient			
4	Wettable Powder	32	5,020	ND	85	40	6,705	
5	in Bulk	60	19,617	32	126	235	25,151	
6		18	4,301	16	165	103	6,201	
7		90	22,606	93	383	578	30,173	
8		294	17,025	78	31	758	21,436	
9		28	599	10	11	85	804	
10	Emulsifiable Concentrate	24	ND	NS	ND	151	0	
11		ND	ND	ND	17	0	85	
12		ND	ND	ND	ND	0	0	
13	Wettable Powder	ND	163	NS	NS	127	330	
14	in Water Soluble Bags	20	89	NS	NS	152	136	
15		ND	4	NS	NS	3	11	
16	Emulsifiable Concentrate	2	1	NS	NS	4	8	
17		ND	ND	NS	NS	3	7	
18			Ambient: 20			ID	125	

ND - None detected (minimum detectable level: 10 ug/m³)

NS - Not sampled (further calculations use an average of like samples)

ID - Insufficient data to calculate

TABLE 2 (Continued, p. 4)

Plot Number	Pesticide Formulation	Work Activity	Skin Area Studied	Minutes of Exposure	Column A		Column B		Column C		Column D		Column E		Column F Total Estimated TOK Dermal Exposure Per Day (Excluding Hand Exposure) (micrograms)				
					Amount of TOK Monitored (ug/cm ²)	TOK Exposure Adjusted To Full Day (ug/cm ²)	Area of Skin Surface (cm ²)		Estimated TOK Exposure Per Day (micrograms)										
							Outside Cloth	Inside Gauze	Covered	Bare	Covered Skin	Bare Skin							
7	Wettable Powder	Mixer/Loader	Head & Neck Anterior	19	0.3743	0.0082	1.1978	0.0262	810				991.44						
				19	0.4053	0.0107	1.2970	0.0342	300					399.37					
				19	0.3743	0.0082	1.1978	0.0262		3,700				96.94					
				19	0.4053	0.0107	1.2970	0.0342		3,300				112.86					
				19	1.7778	0.0527	5.6896	0.1686		2,497.5				421.08					
				19	0.8320	0.0152	2.6624	0.0486		7,030				341.66					
							TOTAL											2,363.35	
						Applicator	Head & Neck Anterior	34	0.3511	0.0036	2.4928	0.0256	810				2,039.90		
							Head & Neck Posterior	34	0.0556	0.0060	0.3948	0.0426	300				131.22		
							Trunk, Anterior	34	0.3511	0.0036	2.4928	0.0256		3,700			94.72		
			Trunk, Posterior	34	0.0556	0.0060	0.3948	0.0426		3,300			141.58						
			Arms and Forearms	34	0.3458	0.0188	2.4552	0.1335		2,497.5			333.42						
			Thigh, Legs and Feet	34	0.7042*	0.0108	4.9998	0.0767		7,030			539.20						
			TOTAL												3,278.13				

* - Sample not taken (value represents an average of like samples)

TABLE 2 (Continued, p. 6)

Plot Number	Pesticide Formulation	Work Activity	Skin Area Studied	Minutes of Exposure	Column A		Column B		Column C		Column D		Column E		Column F Total Estimated TOK Dermal Exposure Per Day (Excluding Hand Exposure) (micrograms)				
					Amount of TOK Monitored (ug/cm ²)	TOK Exposure Adjusted To Full Day (ug/cm ²)	Area of Skin Surface (cm ²)		Estimated TOK Exposure Per Day (micrograms)										
							Outside Cloth	Inside Gauze	Outside Cloth	Inside Gauze	Covered Skin	Bare Skin							
9	Emulsifiable Concentrate	Mixer/Loader	Head & Neck Anterior	18	0.0176	0.0006	0.0581	0.0020	810				48.66						
				Head & Neck Posterior	18	0.0597	0.0007	0.1970	0.0023	300				59.10					
					Trunk, Anterior	18	0.0176	0.0006	0.0581	0.0020	3,700		7.40						
				Trunk, Posterior		18	0.0597	0.0007	0.1970	0.0023	3,330		7.66						
					Arms and Forearms	18	0.0222	0.0004	0.0733	0.0013	2,497.5		3.25						
				Thigh, Legs and Feet		18	0.3618	0.0116	1.1930	0.0384	7,030		269.95				396.02		
					TOTAL														
						Applicator	Head & Neck Anterior	43	0.0475	0.0010	0.2660	0.0056	810				220.00		
								Head & Neck Posterior	43	0.1460	0.0046	0.8176	0.0258	300				253.02	
									Trunk, Anterior	43	0.0475	0.0010	0.2660	0.0056	3,700		20.72		
Trunk, Posterior	43	0.1460	0.0046					0.8176		0.0258	3,330		85.91						
	Arms and Forearms	43	0.0746					0.0016	0.4178	0.0090	2,497.5		22.48						
Thigh, Legs and Feet		43	0.2018					0.0076	1.1301	0.0426	7,030		299.48				901.51		
	TOTAL																		

TABLE 3

ESTIMATES OF SKIN EXPOSURE TO TOK
ON EMPLOYEES' HANDS WHILE
MIXING, LOADING, AND APPLYING TOK
IN MONTEREY AND SANTA BARBARA COUNTIES
OF CALIFORNIA

Plot Number	Pesticide Formulation	Column A		Column B	
		Estimated Exposure Adjusted to Full Day (micrograms)		Total of Combined Operations (micrograms)	
		Mixing and Loading	Application		
4	Wettable Powder	1,062	535	1,597	
5		573	391	964	
6		1,229	1,709	2,938	
7		685	561	1,246	
8		1,015	893	1,908	
9		1,921	1,719	3,640	
10		Emulsifiable Concentrate	134	160	294
11			223	290	513
12	662		3,810	4,482	
13	17,966		NS	19,085	
14	Wettable Powder In Water Soluble Bags	4,460	NS	5,579	
15	Emulsifiable Concentrate	355	NS	1,474	
16		139	NS	1,258	
17		791	NS	1,910	
18		*	*	106	

NS - Not sampled (further calculations use an average of like samples).

* - Combined mixing, loading, and application sample taken.

Field and Application Information for TOK Study Plots in Monterey and Santa Barbara Counties of California

Plot Number	4	5	6	7	8	9	10	11
Pesticide Used	TOK WP 50	TOK WP 50	TOK WP 50	TOK WP 50	TOK WP 50	TOK WP 50	TOK E 25	TOK E 25
Application Rate	6 lb/3 lb a1	6 lb/3 lb a1	7 lb/3.5 lb a1	7 lb/3.5 lb a1	7 lb/3.5 lb a1	6 qt/1.5 qt a1	6 qt/1.5 qt a1	6 qt/1.5 qt a1
Formulation/Active Ingredient	Water	Water	Water	Water	Water	Water	Water	Water
Carrier Used	50 gal	50 gal	60 gal	60 gal	60 gal	60 gal	60 gal	80 gal
Vol. Spray/Acre	Middle	Rear	Rear	Rear	Rear	Middle	Middle	Middle
Tractor Boom Location	8	8	8	8	8	8	8	8
Nozzle Size	550 microns	550 microns	550 microns	550 microns	550 microns	550 microns	550 microns	550 microns
Droplet Size	8"	8"	8"	8"	8"	8"	8"	8"
Height Above Crop	12 mph	12 mph	12 mph	12 mph	12 mph	12 mph	12 mph	10 mph
Speed	300 gal	300 gal	300 gal	300 gal	300 gal	300 gal	300 gal	300 gal
Size of Spray Tank	7 min	7 min	8 min	5 min	8 min	9 min	10 min	9 min
Refill Time	1,500 gal	1,500 gal	1,500 gal	1,500 gal	1,500 gal	1,500 gal	1,500 gal	1,500 gal
Water Tank Capacity of Transfer System	N/A	N/A	N/A	N/A	N/A	12 gal	12 gal	12 gal
Approx. Time To Apply One Spray Tank	55 min	28 min	16 min	18 min	25 min	22 min	35 min	21 min
Mixer/Loader	1	1	1	1	1	1	1	1
Applicators								

Field Crop Information

Crop	Broccoli	Broccoli	Onions	Onions	Onions	Onions	Celery	Celery	Carrots	Celery
Stage of Growth	Post-emergence	Pre-emergence	Post-emergence	Post-emergence	Post-emergence	Post-emergence	Pre-emergence	Pre-emergence	Pre-emergence	Pre-emergence
Climatic Conditions	60°F, Winds to 7 mph	52°F, Winds to 5 mph	59°F, Winds to 7 mph	52°F, Winds to 3 mph	60°F, Winds to 6 mph	58°F, Winds to 10 mph	56°F, Winds to 8 mph	65°F, Winds to 3 mph	56°F, Winds to 8 mph	65°F, Winds to 3 mph
Acres Treated	15	20	14	14	18	38	14	10.5	14	10.5
Drift	None	None	None	None	None	None	None	None	None	None
Distance to Human Habitat	1 mile	.3 miles	.5 miles	5 miles	.5 miles	.2 miles	.5 miles	.4 miles	.5 miles	.4 miles

APPENDIX TWO

Date: 5-27-80
Supersedes: new

TOK(Nitrofen) ON XAD-4 AIR SAMPLE TUBES

SCOPE: This method is for the desorption and analysis of TOK from commercially prepared XAD-4 resin tubes.

PRINCIPLE: TOK will be collected from the air onto XAD-4 resin in the air sample tubes by means of a low volume air sample pump. The TOK is desorbed from the resin with acetone, diluted or concentrated as necessary and analytically determined by electron capture gas chromatography.

REAGENTS AND EQUIPMENT:

1. Acetone, hancegrade.
2. Analytical grade TOK(nitrofen)
3. Approved and calibrated personal-sampling pump.
4. XAD-4 resin tubes, SKC or equivalent.
5. Developing vials with teflon septum caps, SKC #226-02 or equivalent.
6. Tube breaking kit, triangular file, tweezers, paper clip, etc.
7. Assorted volumetric glassware and pipets as needed for standards and samples.
8. Gas chromatograph equipped with electron capture detector.
9. 4 foot x 2mm 4% OV-101 on Chromosorb WHP 100/120 mesh glass column.
10. Suggested starting g.c. parameters with the above column are;
 - a. injector = 250 des. C.
 - b. column = 105 des. C. and 30 ml/min nitrogen
 - c. detector = 300 des. C.

ANAYLSIS:

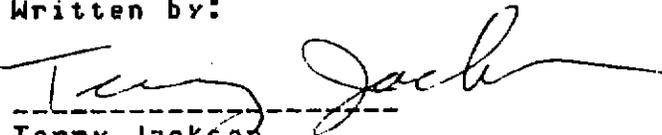
Interferences: High humidity may affect trapping efficiency.

1. Score each sample tube with a file in front of the first section of the resin.
2. Break the tube open.
3. Remove the wire and glass wool, if the formulation used was a wettable powder place the wire and glass wool in a desorption vial containing 2 ml of acetone. Label vial as prefilter.
4. Transfer the first (larger) section of resin and the central foam plug into a desorption vial containing 2ml of acetone and label as front section.
5. Transfer the backup portion of the resin into a third desorption vial containing 2ml of acetone and label as back portion.
6. Place the filled and labeled desorption vials on a sample rotator and rotate for 1 hour.
7. If more than several hours is to elapse before the

REFERENCE:

1. DBCP on Charcoal Tubes, T.Jackson , CDFA Worker Safety method, 7-27-78.
2. Analysis of XAD-4 Resin, T.Jackson, CDFA Worker Safety method, 2-5-76.

Written by:



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APPENDIX FOUR

Date: 5-26 80
Supersedes: none

TOK (nitrofen) IN SOAP AND WATER HANDWASHES

SCOPE: This method has only been checked on water and (Ivory) soap handwashes for TOK on workers' hands.

PRINCIPLE: TOK adhering to the hands of a worker is washed off with a mixture of 250 ml of water (ambient temperature) and one drop of Ivory liquid detergent. The washings are collected and extracted with hexane. The amount of TOK in the extract is determined by electron capture gas chromatography.

REAGENTS AND EQUIPMENT:

1. Hexane, nanograde.
2. Sodium sulfate, anhydrous, granular, Mallinkrodt.
3. 15 ml glass stoppered centrifuge tubes.
4. 4 ml desorption vials.
5. Disposable pipettes and bulbs.
6. Gas chromatograph equipped with electron capture detector.
 - a. 4 foot by 2mm i.d. glass column packed with 1% OV-101 on Chromosorb WHP, or similar.
 - b. Injector at 250 deg. C.
 - c. Column at 195 deg. C. and 30 ml/min. of nitrogen.
 - d. Detector at 300 deg. C.

ANALYSIS:

1. Determine if the submitting agency wishes the results based on the actual volume of handwash received (ppm or ppb) or on total amount of TOK present in the handwash sample. If the results are to be based on the actual volume of handwash received measure the sample in a graduated cylinder and record the volume. Return the sample to the original jar. To sample in jar add about 20 grams of sodium sulfate, and swirl to begin mixing.
2. Add exactly 10 ml of hexane to sample in jar.
3. Tightly cap jar and vigorously shake for one minute. If jar leaks a new liner of aluminum foil or a double liner may be required to seal the jar.
4. Allow mixture to set and separate for 10 to 15 minutes.
5. Using a disposable pipet suction off a portion of the hexane, or hexane-water emulsion into a glass stoppered test tube (round bottom tubes work better).
6. If the emulsion does not break within minutes of placing in the test tube salt the hexane out by adding small amounts of sodium sulfate to the test tube in increments shaking vigorously each time.
7. If desired steps 2 through 6 could be repeated several more times for exhaustive extraction. Preliminary test however, indicated 100% of the TOK recovered in the first extraction.
8. After separation of the hexane from the water transfer the hexane by means of a disposable pipet to a labeled 4 ml desorption vial or similar for storage until assay. Store under

APPENDIX FIVE

Photographs of the TOK worker exposure
study conducted in the Salinas Valley of
California in May and June of 1980.