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RECEIVED for review Februrary 11, 1985. Accepted May 20, 1985.

Optimization of Perchlorination Conditions for Some Representative Polychlorinated Biphenyls

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The yield of decachlorobiphenyl (DCB) from representative Aroclors (50 to 6000 ng) using antimony pentachloride as perchlorinating agent was extremely temperature dependent below 236 °C for a reaction period of 2 h. At 288 °C, a 35-min reaction period was sufficient to obtain DCB yields >80% for Aroclors 1016, 1242, 1254, and 1268. The perchlorination process was shown to be first order. The temperature dependence of the reaction times below 236 °C was largely responsible for the inconsistent perchlorination yields reported previously in the literature. The extraction of DCB with hexane from a HCl-acidified perchlorinated solution and the subsequent column chromatography on silica gel were also essential after the perchlorination to quantitate the DCB by ^{63}Ni electron capture/gas chromatography. The structures of the two nonachlorobiphenyls, which were the penultimate stable intermediates before DCB, were found. The methodology to use the technique for air and blood samples was described.

Polychlorinated biphenyls (PCBs) are ubiquitous in environmental and biological samples (*1-3*). PCBs are usually isolated through hexane extraction of an aqueous sample or after hydrolysis. The extract is then further fractionated by column chromatography and identification/quantification achieved by ^{63}Ni electron capture or Hall conductivity detector gas chromatography (ECD/GC and HC/GC, respectively). For quantifications, at least five major peaks of the original standard are utilized (*4*). However, interfering peaks often make identification and quantification difficult, necessitating more subfractionation. Furthermore, nonstandrd chromatograms may also occur as a result of differential biological metabolism of individual PCB isomers (*5*), differential solubilization of low chlorine-containing PCB isomers in water (*6*), and differential volatilization of the low-chlorine-containing isomers into air (*7*). In addition, industrial capacitors may contain mixtures of PCBs as could spills and hazardous wastes, rendering pattern recognition of complex gas chromatograms an uncertain tool to identify PCBs. Even the Webb-McCall method (*8*) basedon halogen conductivity detector results relies on knowing the PCB type before quantification. Because PCB quality may vary from lot to lot, the original determinations of chlorine content by Webb and McCall (*8*) may only be approximate. Gas chromatograpy/mass spectrometry (GC/MS) identification, though isomer specific, is extremely costly and is best suited for confirmation purposes when levels may be of biological or environmental interest; it is not a routine screening tool.

The major alterntive method is perchlorination (*9-15*) of PCBs to decachlorobiphenyl (DCB). Though isomer specificity is lost, enhanced sensitivity is attained since all PCB isomers are converted to DCB, and the ECD response to DCB is much greater than those for the PCB isomers observed most in samples (tetra-, penta-, and hexachlorinated). Samples have to be split to identify if biphenyl is present since the latter will yield DCB on perchlorination. However, quantitation of only DCB is certainly easier than of four to five isomers and DCB can be readily confirmed by GC/MS. Pattern recognition can then be applied (*3, 16, 17*) to the unperchlorinated sample. If the overall chlorine content can be estimated, the amount of original PCB can be qualitatively found. This is an inexpensive screening method compared with GC/MS analyses.

The key to such a screening method is the quantitative perchlorination of microamounts of PCBs. There are three current reagents: antimony pentachloride (*9-13, 18*), BMC reagent (*9, 10, 15*), and antimony pentachloride–iodine–sulfuryl chloride (*10*). These have been utilized to perchlorinate

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0003-2700/85/0357-2130$01.50/0

>100 mg amounts of PCBs with yields of 85–104%. Berg et al. (*9*) have reported that yields are not dependent on temperature or reaction time. Most of the published micro methods (*9–13 18*) utilize antimony pentachloride at tempertures between 160 and 220 °C, with a range of reaction times between 2 and 15 h. Armour et al. (*12*) obtained yields of 30 to 70% for Aroclor 1242 using the method of Berg et al. (*9*) for which "quantitative perchlorination" was claimed. The modified method of Armour et al. (*12*) though reported to be also quantitative (90–105% yields) is excessively long, tedious, and prone to contamination (*13, 14*). The NIOSH method (*18*) may not be reproducible either (*7*). A micro method using BMC reagent (*15*) appears precise, but the calculated efficiency of perchlorination is between 60 and 70%.

The aim of the present study was to optimize the method of perchlorination of PCBs so that a fast, rapid, precise, and accurate screening method applicable for blood and air samples could be finally evolved.

EXPERIMENTAL SECTION

PCBs. Aroclors 1016, 1242, 1254, and 1268 were chosen as representative PCBs because of chlorine content, past use, and occurrence. These were provided by the U.S. Environmental Protection Agency. The Monsanto lot numbers were C740, C741, K-BO 5-612, and A093, respectively. Decachlorobiphenyl (DCB) obtained frm Ultra Scientific, Inc., was shown to be pure by ECD/GC.

Reagents. The reagents used were antimony pentachloride (Baker), pesticide grade hexanes (Fisher H-300), pesticide grade acetone (Fisher A-40), Type I distilled water (*19*), hydrochloric acid (Fisher A-144), sulfuric acid (Fisher A-300S), potassium dichromate (Fisher P-188), silica gel (Davison, 100/200 mesh, Grade 923), glass wool, and aluminum foil (Kaiser, item 58). The silica gel and glass wool were cleaned by Soxhlet extraction with pesticide grade hexanes for 12 h, then dried at 200 °C for 12 h.

Apparatus. The major apparatus utilized were a calibrated hot plate, a surface thermometer (Spot Check, Model 572F, Pacific Transducer Co.), 22 mL (23 mm × 85 mm) borosilicate glass vials with an aluminum-lined screw cap (Supelco 2-3255), a vortex mixer (Lab-Line Instruments, Inc., Catalog No. 1290). Silica gel columns for column chromatography were produced by vortex-packing 0.5 g of gel into a Pasteur pipet (Fisher 13-678-20B) plugged at the bottom by ca. 6 mm of glass wool. The length of the gel column was 2.6 ± 0.2 cm (arithmetic mean ± standard deviation).

A Hewlett-Packard 5730A gas chromatograph was equipped with a ^{63}Ni-ECD detector. The column was a 2 m × 2 mm i.d. Pyrex column packed with 3% OV-101 on 100/120 mesh Chromosorb W-HP using a flow rate of 25.2 ± 0.4 mL/min of 95/5 argon/methane carrier gas. The temperature of the column, injector, and detector were all 250 °C for DCB analysis. For individual Aroclors, the column temperature was 200 °C.

For GC/MS, a Kratos MS 80 high-performance mass spectrometer was interfaced with a Carlo Erba gas chromatograph. The MS conditions were ionization energy 35 eV, ion current 100 μA, accelerating voltage 4 kV, and resolution 1000. The MS data were acquired and processed on a DS-55 data system using a Data General Nova/4 computer. The GC column was identical with with that used above for ECD/GC. The injector temperature and the separator temperature were 240 °C. Helium was the carrier gas at a flow rate of 26 mL/min.

Optimized Procedure. All glassware was washed in the following manner: the vial was soaked in fresh chromic acid for 15 h and then rinsed 10 times by tap water and then five times by Type I water (*19*). This was followed by five rinsings with pesticide grade acetone. After drying, the containers were rinsed five times with pesticide grade hexanes, before a final drying in a dustless oven.

Since the perchlorination methodology was to be applied at the end of a hexane-extraction step, or after column chromatography using hexane, Aroclor standards in hexane were prepared. A concentrate was first obtained after direct weighing. Dilution to 0.1–6 μg/mL was then performed for all Aroclors, and five concentrations in this range were evaluated in triplicate. This brackets the Aroclor level expected after 8 h of sampling at the

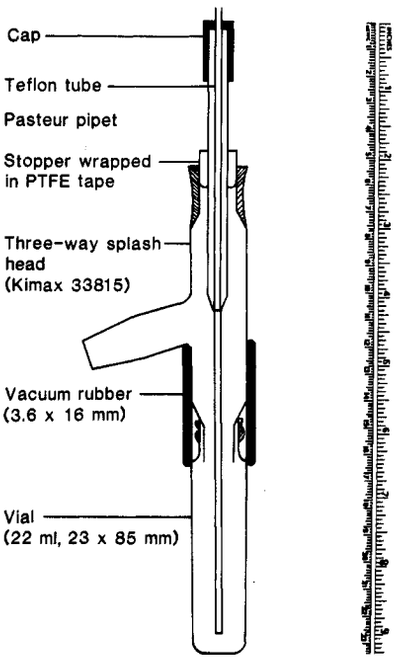

Figure 1. Hexane evaporation apparatus.

permissable exposure level (PEL) set by the Occupational Health and Safety Administration (OSHA) for Aroclors 1254 and 1242, using a Florisil adsorbent, and then desorbing with hexane (*18*). A 0.5-mL aliquot was placed in the 22-mL vial. This was connected to a three-way splash head (14/20 Kimax 33815) by vacuum rubber tubing (3.6 cm long × 1.6 cm i.d.). A stopper wrapped in PTFE tape and containing a Pasteur pipet (Fisher, 13-678-20D) was inserted so that the tip of the pipet was 5 cm from the vial bottom. This constant geometry was maintained for all solvent evaporations. The apparatus is depicted in Figure 1. The Pasteur pipet was connected to a cylinder of compressed nitrogen, the nitrogen passing through silica gel desiccant (Davison 100/200 mesh grade 923) and molecular sieves (Fisher M-237) to purify the gas. A rotameter was placed in line just before the vial to measure flow rates. The flow rate of nitrogen was 0.29 ± 0.01 L/min. The exit end of the splash head was vented through a trap and a large charcoal tube which was connected also to an operating aspirator (Fisher 09-960-2). This was done for safety and disposal reasons. The hexane was evaporated just to dryness (5 min). A 0.5-mL aliquot of antimony pentachloride was pipetted into the vial. The vial opening was then covered by aluminum foil with the dull side facing the sample. A screw cap lid lined with aluminum foil was screwed on tightly just to finger tightness. The vial was wrapped inside a strip of aluminum foil and was, then, placed on a preheated hot plate held at 288 ± 2 °C (mean ± standard deviation). After 35 min, the perchlorinated sample was cooled to room temperature (3–4 min). A 0.5-mL aliquot of 30% HCl (v/v) was then added dropwise with shaking. The vial was shaken gently, capped loosely, and allowed to stand until the reactants cooled (3–4 min). The cooled sample was vortex extracted (10 s) by hexane (4 × 2 mL). When the two layers settled and the upper layer lost opacity, the supernatant was transferred to a silica gel microcolumn, previously eluted with 1 mL of hexane. Each hexane extract was placed separately onto the column. An additional 2 mL of hexane was used to rinse the vial, the Pasteur pipet, and the microcolumn in that order. All the eluates were progressively collected in a 10-mL graduated cylinder or a 22-mL vial. The total volume of sample was adjusted to 10 mL. Some samples were either diluted or concentrated (solvent evaporation by nitrogen) for determination in the linear range of ECD/GC (202 to 3480 pg of DCB). A 4.8-μL aliquot was injected into the gas chromatograph, and the amounts were calculated from the external standards calibration.

Application to Air and Blood Samples. *Air Samples.* During a spill of Aroclor 1254, a personal air sampler using 100 mg/50 mg sections of water-deactivated Florisil (3% w/w; 30/48 mesh) under the conditions described by NIOSH (*18*) was used to monitor personnnel during clean-up operations. The samples

Table I. Perchlorination Efficiency of Various Amounts of Aroclors by the Optimized Method[b]

Aroclor	amt of Aroclor, ng	% recovery[a] (mean ± std dev)	grand mean ± std dev
1016	77.8	95 ± 1	91 ± 4
	181	86 ± 5	
	352	91 ± 8	
	442	92 ± 14	
1242	60.4	99 ± 6	88 ± 8
	302	84 ± 2	
	1208	81 ± 0	
	6040	88 ± 6	
1254	55.8	90 ± 12	95 ± 5
	83.7	92 ± 3	
	112	97 ± 8	
	446	98 ± 7	
	2790	93 ± 8	
	5580	102 ± 4	
1268	79.8	84 ± 2	93 ± 9
	530	87 ± 3	
	1230	101 ± 1	
	5330	100 ± 4	
mean ± std dev			92 ± 7

[a] Triplicate samples in each group. [b] ANOVA: types of Aroclor (A) d.f., 3; SS, 137.8; MS, 45.9; F, 1.15; $F^{0.05}_{crit}$ 3.34; within types (error) d.f., 14; SS, 557.3; MS, 39.8.

were desorbed with 5 mL of hexane (*18*) and then the hexane extract was split in half. A 4–8-μL aliquot from one half was injected directly for Aroclor 1254 analysis. The other half was placed in the 22-mL vial of Figure 1 and the hexane evaporated as above before perchlorination. The levels of the split samples were compared after the DCB content was corrected for Aroclor 1254 chlorine content.

Blood Samples. A 10-mL blood sample of a worker who was allegedly exposed to an unknown PCB was taken for analysis using the technique of Que Hee et al. (*20*). The hexane extract (10 mL) at the end of the procedure in ref 20 was then split into four. One sample was injected directly to assess if pattern recognition could identify the PCB. The chromatograms were so complex that no pattern was discernible. This also occurred after one evaporated sample was perchlorinated; there were many peaks in the DCB area.

The remaining three samples were further subjected to silica gel chromatography as described in ref 20. The 140-mL hexane eluates were evaporated to 10 mL by nitrogen. One of the samples was injected into the gas chromatograph directly for PCB analysis, and one other sample was perchlorinated as above after evaporation. Again, in both samples no PCBs could be discerned because of the complexity of the chromatograms, even though the chromatograms were less complex than before. The two remaining silica gel treated samples were both evaporated to 2 mL, and then both subjected to further column chromatography on 1 g basic alumina columns (Brockman Activity I, 80/200 mesh (Fisher A-941), Soxhlet extracted with hexane for 24 h, and dried overnight at 150 °C), contained in a Pasteur pipet. A washed glass-wool plug supported the alumina. The columns were subjected to a hand column vibrator for 10 s. A quarter inch layer of Ottawa sand (MCB SX 70 CB666) was placed on top of the column. The microcolumn was clamped vertically and washed with 5 mL of hexane. The samples were then chromatographed, and 20 mL of hexane eluate containing the PCBs was collected. The samples were split in half. An aliquot from one half was injected for PCB analysis by gas chromatography, and again the patterns were still too complex to assign the type of PCB. The remaining halves were perchlorinated after evaporation. In both samples, a symmetrical peak at the retention time of DCB was found. GC/MS confirmed this to be DCB. GC/MS analysis of the concentrated unperchlorinated eluates from the alumina column showed no biphenyl to be present and that some peaks contained PCBs, though still unresolved from other compounds.

RESULTS AND DISCUSSION

The yield of DCB for each of the Aroclors analyzed in triplicate by the optimized method for various starting amounts is provided in Table I. The overall arithmetic mean ± standard deviation was 92 ± 17% for starting amounts of 56 to 6000 ng of various Aroclors. The entire analysis procedure was completed within 2 h.

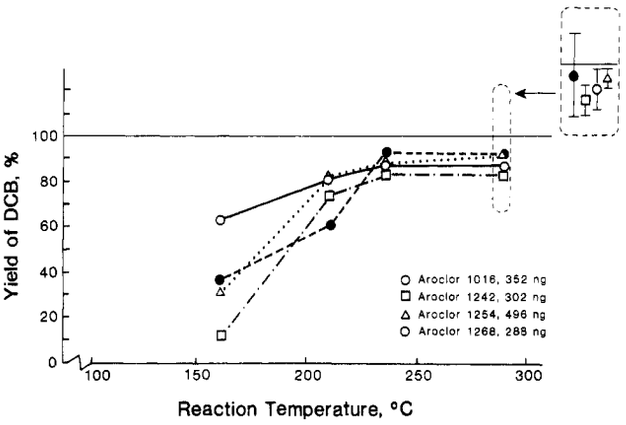

Figure 2. Dependence of DCB yield with temperature based on 2-h perchlorinations.

The optimized technique was developed after lengthy preliminary studies. These studies are summarized next.

Temperature Dependence. Figure 2 gives the temperature dependence of the reaction for 2 h heating duration. Above 236 °C there was a constant high DCB yield but below this value the reaction was much affected by temperature. This contradicts the work of Berg et al. (*9*). The appearance of other peaks in the chromatograms <236 °C also confirmed the presence of intermediates. When a sample that was perchlorinated at low temperature was reperchlorinated at 288 °C, the yields were again quantitative. The early eluting peaks also disappeared from the chromatogram. The yields also increased on allowing the solution to stand at room temperature for 3 days though they were not quantitative.

At temperatures <236 °C, a compound eluting with a relative retention time (RRT) of 1.6 relative to DCB was observed, though not for Aroclor 1254, and was consistent with bromononachlorobiphenyl (*13*, *14*). It was not present after reaction at 288 °C. Therefore, perchlorinating at 288 °C ensures a minimal bromononachlorobiphenyl peak, a problem noted by many investigators (*8–15*). Two other compounds with RRTs of 0.62 and 0.84 were also present <236 °C but not at 288 °C. GC/MS analysis indicated they were nonachlorobiphenyls (*3*). By considering their Kovats retention indexes (*21*) and comparing Sissons and Welti (*22*), the first peak was the 2,2′,3,3′,4,5,5′,6,6′-isomer and the latter was the 2,2′,3,3′,4,4′,5,5′,6-isomer. These isomers, not previously reported in other studies, were thus the penultimate stable intermediates before DCB itself and indicate the presence of at least two mechanistic routes to DCB. At 161 °C for Aroclor 1242, the half conversion times to DCB were computed to be 3.5 and 3.9 h, respectively, assuming first-order kinetics and the response factors obtained by Mullin et al. (*23*). Thus, the temperature dependence appeared to account for much of the contradictory nature of the literature relative to DCB yield, since most of the methods utilizing antimony pentachloride were done around 161 °C for varying periods of time.

Assuming the perchlorination process to be first order in the presence of excess antimony pentachloride (shown directly by time experiments and varying the amount of antimony pentachloride), an Arrhenius treatment (log (rate constant) vs. 1/temperature (K)) showed (*24*) that the activation energies for perchlorination of Aroclors 1016, 1242, 1254, and 1268 were −59.1, −43.2, −46.8, and −21.7 kJ/mol, respectively (Table II). These activation energies are generally inversely proportional to chlorine content, with those for Aroclors 1242

Table II. Activation Energies and Half-Conversion Times for the Perchlorination of Various Aroclors Using a 2-h Reaction Time

Aroclor	activation energy,[a] kJ/mol	half-conversion time,[b] h			
		161 °C	210 °C	236 °C	288 °C
1016	−59.1	2.99	1.42	0.45	0.73
1242	−43.2	7.77	0.99	0.75	0.75
1254	−46.8	3.67	0.76	0.59	0.49
1268	−21.7	1.39	0.80	0.61	0.54

[a] Found by a Arrhenius plot (*24*). [b] Assuming first-order kinetics.

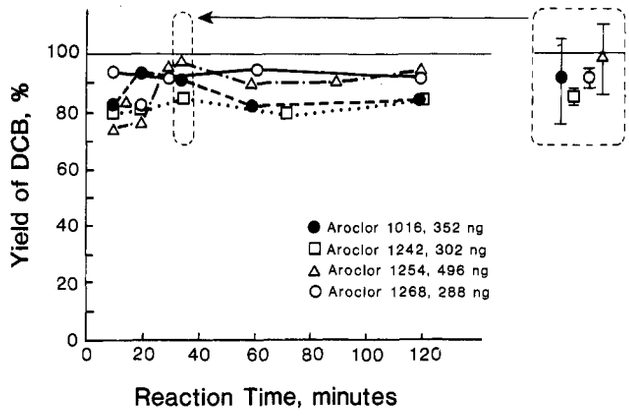

Figure 3. Dependence of DCB yield on reaction time at 288 °C.

and 1254 not differing significantly. These data have not been reported previously. Half-conversion times were calculated for the Aroclors at each temperture assuming a first-order process (Table II). This shows that Aroclor 1242 required much more reaction time than the others for complete perchlorination at 161 °C, a temperature used most often by other investigators. This might explain why yields for Aroclor 1242 have been so variable at this temperature (*12*). At 210 °C, Aroclor 1016 was hardest to perchlorinate. However, above 236 °C, the half-conversion times for all the Aroclors were less than 0.75 h. The mean half-conversion time at 236 °C or above was 0.61 ± 0.12 h (mean ± standard deviation). These results support the contention that nonoptimal reaction times could have contributed to the variability of the perchlorination yields reported in the literature for the antimony pentachloride technique.

Reaction Time. Setting 288 °C as the optimum temperature, reaction times were varied from 10 min to 2 h. The results are provided in Figure 3. There appeared to be no dependence on reaction times between 35 and 120 min for all the Aroclors. A time of 35 min was thus chosen as the optimal time which allowed fast quantitative reaction.

Optimization of Solvent Evaporation Time. Unevaporated Aroclor samples diluted to a given volume were compared by ECD/GC with evaporated Aroclors dissolved in the same volume to assess the optimum evaporation time for the initial hexane solutions. Each Aroclor solution had to be evaporated just to dryness. To obtain reproducible evaporation times, the geometry and flow rates within the evaporating apparatus had to be constant (Figure 1). Perchlorination of partially evaporated solutions was always attended by the presence of carbon granules in the perchlorinated solutions and low DCB yields.

Column Chromatography. To obtain the optimum eluting volume, the eluate was monitored by ECD/GC. This was also repeated for known concentrations of authentic DCB as well as for the perchlorinated Aroclors. The perchlorinated Aroclors and DCB alone eluted in the same eluting volume. Various heights of silica gel were also evaluated. When no column chromatography was done, the ECD/GC step was impossible because of the presence of much electron capture sensitive material which caused the detector to be irreproducible for days.

Hexane Extraction from 30% HCl. Five extractions using 2 mL of hexanes and 1 mL of hexanes were performed. Volumes of 2 mL allowed complete partitioning in two extractions. Deletion of this step led to no peaks on ECD/GC since the acid hydrolysis was necessary to release DCB so it could be extracted in the hexane layer.

Cleaning of Glassware. The acetone rinse was absolutely essential to obtain quantitative yields in chromic acid washed glassware. Without the acetone step, the yields were around 47%. The extensive washing with tap and distilled water was also essential to obtain yields >80%. The lower yields were caused by chromium on the glass walls leaching into the antimony pentachloride and inhibiting the reaction. Washing glassware with just hexane ten times caused yields of around 83%. However, in PCB contaminated glassware, washing with hexane alone was not effective.

Closed vs. Open Perchlorinating Systems. The volume of the vessel did not appear to be critical as long as the optimal conditions were used. This is probably caused by the fact that the aluminum film upon which the screw-cap screws down effectively sealed the vial. However, heating the totally immersed vial in a sand bath (*18*) caused lower yields. Since closed vessels appeared to produce lower yields, the hot plate mode of heating may be effective because of the refluxing aspect of the system.

Other Studies. To assess the possible influence of the perchlorination matrix on the recovery of DCB, known amounts of DCB (0, 85, 170, 254, and 339 ng) were added to perchlorinated Aroclor 1254. The slope for the standard additions experiment was identical with that for an external standards calibration. Thus, the recovery of DCB was at least 91%, comparing the two slopes. This answer was statistically insignificant from the mean perchlorination efficiency for Aroclor 1254 (Table I).

Conversion from DCB to Aroclor Content. To convert DCB content to Aroclor content, the DCB content must be multiplied by (% chlorine content of Aroclor)/(% chlorine content of DCB). In all cases, the observed Aroclor content agreed with the known Aroclor content (Aroclors 1016, 1242, 1254, and 1268 had observed values that agreed to 96 ± 11, 88 ± 8, 97 ± 9, and 95 ± 11, respectively (arithmetic mean ± standard deviation)).

When the results of Takamiya (*15*) for Kanechlors 300, 400, 500, and 600 were treated in this manner, the agreement was generally less than 80% (58, 68, 70, 79%, respectively) and indicates that the perchlorination procedures were not optimal.

Studies on Air and Blood Samples. Application to air samples was easiest. The DCB levels corrected for chlorine content agreed with those calculated by the Webb-McCall method (*8*) but not by the NIOSH multiple peaks method (*18*). The reasons for this will be given in another publication.

The blood sample required an alkaline hydrolysis, hexane extraction and silica gel column chromatography (*20*), and an additional alumina column chromatography step before perchlorination was effective as a screening technique. This procedure still did not allow pattern recognition of the unperchlorinated half sample and so use of the screening method is favored because of its greater sensitivity and as an indication if further chromatography of the unperchlorinated half sample is worthwhile.

ACKNOWLEDGMENT

The Quality Assurance Division, EMSL–Las Vegas, U.S. Environmental Protection Agency is thanked for the gift of

the Aroclors. Koka Jayasimhulu is thanked for performing the GC/MS analyses.

Registry No. DCB, 2051-24-3; $SbCl_5$, 7647-18-9; Aroclor 1016, 12674-11-2; Aroclor 1242, 53469-21-9; Aroclor 1254, 11097-69-1; Aroclor 1268, 11100-14-4.

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RECEIVED for review March 25, 1985. Resubmitted May 20, 1985. Accepted May 20, 1985. This work was presented at the 187th American Chemical Society Meeting, April 8-13, 1984, St. Louis, MO, as ENVR 20. ES000159 was partially responsible for financial support. J. M. Lin was the recipient of a graduate assistantship in the Department of Environmental Health.

Infrared Analysis of Refined Uranium Ore

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Infrared assay of refined uranium ore (yellowcake) is described and the results are related to worker protection measures. Eleven standard mixtures of ammonium diuranate and U_3O_8 were prepared that contained 0% ammonium diuranate (pure U_3O_8) through 100% ammonium diuranate (no U_3O_8) in 10% intervals. Assay of these mixtures (0.30% in KBr) showed that ammonium diuranate could be accurately assayed within ±7% standard error of the mean (n = 8) and U_3O_8 to within 12%. For specimens that contained only one of the uranium forms, the percentage of ammonium diuranate was overestimated by 16 ± 4% and U_3O_8 was underestimated by 24 ± 2%. Fifty-six commercial samples from 10 mills were assayed. The results were applied to the use of urinalysis data to estimate the amount of uranium in the body of a worker after a hypothetical inhalation of dust from an assayed sample. It was shown that the uncertainty in body burden estimates could be reduced from a factor of 100 to a factor of 10 with 95% confidence. Infrared assay results also showed that the ammonium diuranate and U_3O_8 content of a specific yellowcake sample cannot be predicted from the dryer temperature alone.

Uranium ore is refined in uranium mills to produce the commercial product known as yellowcake. Processes vary among mills, but three basic steps are commonly used: leaching of crushed ore, recovery of leached uranium, and drying of product for packaging. Leaching is accomplished with H_2SO_4 or $Na_2CO_3/NaHCO_3$ solutions. Uranium dissolved in H_2SO_4 is removed by solvent extraction or ion exchange and precipitated from solution by ammonia, as ammonium diuranate. Ammonium diuranate (often written as $(NH_4)_2U_2O_7$) is actually a variable mixture of $UO_3 \cdot xNH_3 \cdot yH_2O$ compounds with their composition dependent on the pH during precipitation. Four stoichiometric forms can be crystallized by shaking under an ammonia atmosphere for 2 weeks (*1*); but these conditions do not occur in industry. Uranium dissolved in $Na_2CO_3/NaHCO_3$ is precipitated by NaOH. Sodium diuranate is generally dissolved and reprecipitated by ammonia. Prior to packaging, ammonium diuranate precipitate is dried at temperatures chosen to either dehydrate it or convert it to U_3O_8. Partial or incomplete conversion often occurs.

Both ammonium diuranate and U_3O_8 are potentially toxic, if inhaled, requiring that dry yellowcake packaging be done under regulations that specify ventilation equipment and other safety measures to protect workers. Because ammonium diuranate is more soluble than U_3O_8 (*2-5*) and dissolved uranium in the form of UO_2^{2+} is absorbed into blood and excreted in urine, chemical toxicity to kidney and accumulation in bone are possible. Dissolution and excretion of U_3O_8 also occur, but at a much slower rate, so that gradual accumulation of U_3O_8 in lung could also deliver an appreciable radiation dose.

Routine urinalysis for uranium is used to monitor protection measures so that workers who might inhale yellowcake dust do not accumulate dangerous amounts of internally deposited uranium. It is necessary, then, to quantitatively measure ammonium diuranate and U_3O_8 in yellowcake to interpret urinalysis data, either as part of routine monitoring or as an evaluation technique for accidental exposures. Dissolution studies in vitro are useful for studies of a few selected samples, such as a sample of a lot involved in an accident, but they are too time-consuming for use in a survey of yellowcake samples

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