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Determination of Part-per-Trillion Concentrations of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Fish

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An analytical procedure has been developed and utilized for the determination of approximately 10 to 100 parts per trillion (10<sup>-12</sup> g/g) concentrations of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in fish. The technique involves digestion and extraction of the matrix followed by a series of adsorbent, and chemically-modified adsorbent, liquid column chromatographic clean-up steps. A final “residue polishing” step via elevated temperature reversed-phase high performance liquid chromatography is applied prior to detection by multiple ion mode gas chromatography-mass spectrometry. Using 13C-labeled extraction of the matrix followed by a series of adsorbent, and dioxin (TCDD) in fish. The technique involves digestion and the determination of approximately 10 to 100 parts per trillion concentrations. Relative to this range, TCDD recovery is 75% ± 25%, and the precision of a single determination at the 95% confidence level (2σ) is ±20% relative at 50 ppt TCDD concentration.

One compound which has been the subject of intense analytical and toxicological investigations in recent years is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). As a result of the presence of TCDD as a contaminant in 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) and related ester herbicides and phenoxy acetic acid (2,4,5-T) and related ester herbicides and many reports have discussed both the determination of this compound and its biological activity. Much of the work up to 1974 is contained in (1), while work since that time is more scattered through the literature. Co-workers have described methods and their application to the determination of part-per-trillion (ppt, g/g) level in a variety of environmental matrices using gas chromatography-mass spectrometry (GC-MS) (2-9). O’Keefe, Meselson, and Baughman (10) have recently described a neutral clean-up procedure for this determination in milk. A similar method has been described by Fukuhara et al. for low amounts of TCDD in seafoods (11). Workers at the National Institute for Environmental Health Sciences (12) have also described a procedure which utilizes negative chemical ionization GC-MS which apparently yields high sensitivity. In all the above methods, however, the presence of other lipophilic substances represents a severe limitation. As Hummel (3) has pointed out, many commonly-observed environmental pollutants can be interferences. As part of an investigation into the presence of some halogenated aromatic compounds in fish and water, we have analyzed a variety of fish for the presence of polychlorinated biphenyls (PCB), polybrominated biphenyl (PBB), 4,4′-dichlorodiphenylethylene (DDE), and TCDD.

In order to avoid interference from million-fold excess concentrations of these materials, we have developed a multistep clean-up procedure which is very effective at removing these halogenated aromatic compounds as well as yielding high recovery and good precision for TCDD.

EXPERIMENTAL

Apparatus. As described by us and co-workers (6, 9), we have utilized low resolution GC-MS for the primary determination, with GC-high resolution MS for confirmation of identity. These low resolution GC-MS determinations were performed on a Hewlett-Packard model 5992A (400 resolution) equipped with a single-stage jet separator using helium at 20 cm<sup>3</sup>/min. for the carrier gas. The GC column was a 210-cm by 2-mm (i.d.) glass column packed with 0.6% OV-17/0.4% Poly S-179 on a specially deactivated Chromosorb W-AW (80/100) support. The final cleanup is achieved on a liquid chromatograph consisting of an Altex Model 110 pump, Rheodyne Model 7120 injector valve with 20-μL loop, a 250 mm × 4.6 mm DuPont Zorbax ODS column and a Perkin-Elmer LC-55 variable wavelength detector, using methanol as the mobile phase.

These analyses at ppt levels require careful attention to the purity of all reagents. The procedures described here include provision for cleaning adsorbents and reagents to remove traces of phthalate plasticizers and miscellaneous chlorinated organic compounds.

Reagents. 44% Sulfuric Acid on Silica. Chromatographic grade sulfuric acid as 100/200 mesh Bio-Sil A is initially dried in a glass tube furnace for ~30 min at 180 °C under a continuous dry nitrogen purge. It is then removed from the furnace and cooled to ambient temperature, and subsequently rinsed with consecutive ~75-mL portions of methanol and methylene chloride (Burdick and Jackson distilled-in-glass quality). The methylene chloride saturated material is returned to the tube furnace which has been set to 50 °C and the dry nitrogen purge reestablished. Over a period of ~25 min the furnace temperature is increased in a step-wise manner to 180 °C. This technique can be described as a modified sweep co-distillation of the adsorbent using methylene chloride saturated nitrogen, and has been found to be an effective means for trace contaminant removal from silica. The effluent gases from this operation must be vented to a fume hood. The silica is then activated for an additional period of ~90 min at 180 °C. Dried adsorbent is cooled and placed in an appropriately sized glass bottle. Sufficient concentrated sulfuric acid is added directly to the silica to yield an acid concentration of 44% based upon total weight. The material is manually shaken until no clumping can be observed, and is then transferred to a glass bottle and stored in a desiccator over phosphorous pentoxide until used. Caution: This reagent retains all of the properties of concentrated sulfuric acid, and should be handled accordingly.

10% AgNO<sub>3</sub> on Silica. The silica support for this reagent is 100/200 mesh Bio-Sil A, solvent rinsed and activated by the procedure described for 44% sulfuric acid on silica. Activated silica is placed in an appropriately sized glass bottle and its weight determined. Using the support weight, the amount of silver nitrate necessary to yield 10% by weight based on the resulting total weight is calculated. Similarly, a second calculation is made to determine the amount of de-ionized water necessary to yield 30% by weight based upon the total weight of silica and water only. In accordance with the determined quantities, the silver nitrate is dissolved in de-ionized water. This solution is then added to the activated silica in a stepwise fashion with shaking to produce a uniformly coated, free-flowing powder. The material is then allowed to stand for a minimum period of ~30 min, after which it is placed in a glass tube furnace set at ~70 °C under a continuous dry nitrogen purge. In a stepwise manner over a period of ~5 h the temperature of the furnace is increased to 120 °C. Provisions should be made to permit condensate to drain from the exit port during this phase of the preparation. From the point that condensation ceases, the adsorbent is activated for an additional period of ~15 h at 125 °C. The finished product is stored in an amber glass bottle in a desiccator over phosphorus pentoxide until used.

Basic Alumina. Chromatographic grade aluminum oxide as 100/200 mesh Bio-Rad Basic Alumina AG-10 is initially dried in a glass tube furnace for ~60 min at 300 °C under a continuous dry nitrogen purge. In order to avoid interference from million-fold excess concentrations of these materials, we have developed a multistep clean-up procedure which is very effective at removing these halogenated aromatic compounds as well as yielding high recovery and good precision for TCDD.
dry nitrogen purge. It is then removed from the furnace, cooled to ambient temperature, and rinsed with ~150 mL of methylene chloride. The methylene chloride saturated material is returned to the tube furnace (again set at 50 °C) and the dry nitrogen purge reestablished; over a period of ~25 min the furnace temperature is increased to 180 °C and this temperature is maintained until solvent condensation at the exit port ceases. Effluent gases must be vented to a fume hood. The basic alumina is then activated for an additional period of ~90 min at 300 °C. Activated adsorbent is stored in a glass bottle in a desiccator over phosphorus pentoxide until used.

Other Reagents. All solvents are Burdick and Jackson, distilled-in-glass quality which are tested by submitting them to the procedure described to verify absence of contamination. Laboratory chemicals, (H$_2$SO$_4$, KOH, AgNO$_3$) were ACS reagent-grade (J. T. Baker) and are also checked for background contamination.

One reagent found to be of inadequate purity for these analyses is the pre-purified nitrogen used to reduce the volume of various solvents. When various grades of cylinder nitrogen or air are used to reduce 25 mL of hexane to dryness, severe contamination is observed. This is corrected by the use of a specially-designed gas purification system which consists of a series of packed traps which contain: 10% Aplienon L plus 10% each micronized Carbopack B (Supelco) and Amoco PX-21 active carbon on 60/80 Chromosorb W-AW; 15X molecular sieve, 80/100 mesh; 20% H$_2$SO$_4$ on 100/200 Bio-Sil A (Bio-Rad Laboratories, Richmond Calif.); 80/100 mesh Carbosieve S (Supelco Inc., Bellefonte, Pa.). These materials are packed into 10 cm x 1 cm (i.d.) tubes and connected in series in the above order. When nitrogen gas is passed through these to concentrate common solvents 1000-fold (10 mL to 10 µL), the resulting electron-capture gas chromatogram is free of all interfering peaks in the region of TCDD elution and beyond.

Procedure. Sample Preparation and Cleanup. The sample preparation procedure consists of four basic parts: (1) sample digestion and extraction to remove the bulk of the sample matrix and to transfer the pesticide residue fraction into a suitable solvent, (2) removal of lipids through reaction with oxidizing reagents, (3) separation of TCDD fraction from common chemical interferences (PCB, DDE), and (4) a final high performance liquid chromatographic (HPLC) cleanup to provide additional removal of contaminants (i.e. PCBs, DDE, phthalates) and to remove compounds which are very similar to dioxins (chlorinated benzy]l-phenylethers) (13).

A 10-g portion of fish (flesh, viscera, or whole-fish homogenate) is mixed with 20 mL of ethanol and 20 mL of 40% aqueous KOH. The homogenized sample is then adjusted to 100 mL and centrifuged at 4000 rpm for 10 min. The supernatant is removed and a 10-mL portion of pre-reduced methylene chloride is added. The solution is centrifuged at 4000 rpm for 10 min. The supernatant is removed and the residue is dried under N$_2$. The residue is dissolved in 10 mL of isooctane.

Figure 1. Multi-ion chromatogram of control trout spiked with 30 ppt TCDD. Sample concentrated 500X. Ions monitored and full-scale intensities as shown. TCDD retention time was 4.6 min to elute the TCDD from the AgNO$_3$/silica, and the eluent is collected on the top of the basic alumina column. Fifty milliliters of 50% (v/v) carbon tetrachloride in hexane is washed through the basic alumina column followed by 10 mL of hexane. The TCDD is finally removed using 20 mL of 50% (v/v) methylene chloride in hexane. This column system provides the basic separation of TCDD from some common pesticide residues. The AgNO$_3$/silica is effective in removal of DDE, chlorinated aliphatic hydrocarbons, and sulfides. The basic alumina column primarily separates PCBs from the TCDD-containing fraction.

The final step in the clean-up scheme is a reversed-phase HPLC separation. This step is used solely as a clean-up step; and, even though an ultraviolet detector is used to monitor the column effluent, no attempt is made to quantitate during this step. After evaporation of the methylene chloride–hexane eluate, the residue (generally not visible) is dissolved in 10 µL of chloroform. The entire 10 µL is charged into the 20-µL loop of the HPLC injection valve and the final cleanup made, collecting the TCDD fraction between 4.3 and 5.3 min. Recovery of TCDD from the methanol eluate is facilitated by collecting the TCDD fraction in a 10-mL volumetric flask previously charged with 1.5 mL hexane. After the desired 2-mL fraction has been collected, the addition of an aqueous 1% so1Fum bicarbonate solution to the flask followed by gentle shaki. allows the collection of the hexane extract as the upper layer for evaporation and final GC-MS determination.

Sample Determination and Calculations. The sample residue is dissolved in 10 to 20 µL of isooctane immediately prior to analysis. (Various phthalates which are ubiquitous contaminants of most bottle caps and septa may be avoided by minimizing the length of time sample solutions are allowed to stand prior to injection.) Using the chromatographic conditions described earlier, the analysis is achieved by monitoring the following ions: 319.9, 321.9 and 323.9 amu for the molecular-ion cluster of native TCDD and 331.9 amu as the most intense ion of the molecular ion cluster of $^{13}$C enriched TCDD (14). Figure 1 shows the MID chromatogram from a control trout homogenate to which has been added 30 ppt of native TCDD and 500 ppt $^{13}$C-TCDD. Also shown are the full-scale intensities (computer-controlled to keep the largest
Table I. TCDD Determination in Control Trout Homogenate

<table>
<thead>
<tr>
<th>sample no.</th>
<th>results, ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ND(20)*</td>
</tr>
<tr>
<td>2</td>
<td>ND(10)</td>
</tr>
<tr>
<td>3</td>
<td>ND(4)</td>
</tr>
<tr>
<td>4</td>
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<tr>
<td>5</td>
<td>ND(12)</td>
</tr>
<tr>
<td>6</td>
<td>10(10)</td>
</tr>
<tr>
<td>7</td>
<td>14(14)</td>
</tr>
</tbody>
</table>

Mean = ND(11) ppt ± 5 ppt (std. dev.)

* ND(xy) indicates that the compound was not detected with a limit of detection of xy. AB(xy) indicates that an amount AB of TCDD was detected, with a detection limit of xy.

peak on-scale) of the GC-MS. The peak height multiplied by the full-scale factor corresponds to the total intensity of that ion. The equation shown below was then used to calculate the apparent concentration of TCDD.

\[
\text{TCDD concn, ppt} = \frac{A}{B} \times C \times \frac{V}{W} \times \frac{1}{[(D \times E)/(F \times G)]} \times 1000 (1)
\]

where the symbols are defined as follows:

- A: the peak height of native TCDD in the sample times the attenuation factor
- B: the peak height of native TCDD in the standard times the attenuation factor
- C: the concentration of the standard, ng/mL
- V: final volume of the sample extract, mL
- W: initial sample weight, g
- D: the peak height of the internal standard in the sample at m/e 332 times the attenuation factor
- E: the concentration of the internal standard in the standard solution, ng/mL
- F: the peak height of the internal standard in the standard solution, at m/e 332, times the attenuation factor
- G: the weight of internal standard added to the sample divided by the final volume of the sample, ng/mL

The term enclosed in brackets \([(D \times E)/(F \times G)]\) × 100% is the recovery of the internal standard that had been added to the sample before workup.

RESULTS

Validation Data. The method was validated by determining the precision and accuracy on samples fortified with known concentrations of TCDD. The accuracy was studied as a function of TCDD concentration by spiking control fish at levels of 1X, 3X, and 10X of the estimated limit-of-detection (LoD) of the method. The LoD was determined by analyzing seven portions of homogenized trout control. Table I shows the results of the analysis of these controls.

Based on a 10 ppt LoD, portions of the same control homogenate were spiked with native TCDD at levels of 10, 30, and 100 ppt and were analyzed according to the procedure described. The results obtained from the recovery experiments are shown in Table II.

These data show the futility of trying to analyze at the limit of detection. They also demonstrate the expected improved precision at concentrations much higher than the limit of detection.

The precision of the method was demonstrated by analyzing seven portions of a trout homogenate which contained apparent TCDD residues. The results are shown in Table III. Although the uncertainty associated with the mean of the internal standard recovery is greater than that of the native TCDD determinations, these values are typical of those obtained in these determinations and point out the advantages to be gained from the use of an internal standard.

DISCUSSION

This work indicates the value and necessity of multicolumn, multiadsorbent procedures for the determination of ultra-trace amounts of organic compounds in environmental samples. When these steps are used, it becomes increasingly important to monitor the recovery of solutes of interest through the whole procedure. The use of an isotopically-labeled form of the solute offers considerable advantage in this respect.

This work also reveals the value of a well-designed validation sequence. The examination of seven controls, seven replicate samples, and seven spiked samples allow a fairly good evaluation of the method performance and the determination of the “limits of detection”. Although this is not as rigorous as the “ten-ten-ten” procedure described by Harris and Cummings (15), it does reveal the dependence of precision and recovery. In this work, we have defined “limit of detection” (LoD) as the concentration at which the measured signal (TCDD MID peak height) is 2.5 times the noise (ion intensity of the same mass at other retention times or the ion intensity at the same mass at the same retention time for known control samples). Although there have been many different ways to define LoD, for these types of analyses, this procedure contains some replicate samples to allow calculation of confidence intervals while recognizing the nonhomogeneity of environmental samples and not placing inordinate demands on analysis time or effort.

A comparison was made of the relative efficiencies of this clean-up method and that previously described by co-workers (6) for the analysis of fish samples heavily contaminated with DDE and PCBs (estimated 1–10 ppm each in the original sample). The latter method has been in use at Dow for approximately four years and has been widely accepted by the outside scientific community as being very reliable for the determination of TCDD at ppt-levels in a wide variety of sample matrices. Comparison mass chromatograms are shown in Figure 2. In each chromatogram, the top trace is the

Table II. Recovery of Native TCDD from Trout

<table>
<thead>
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<th>sample</th>
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<th>recovery, %</th>
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</tr>
<tr>
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</tr>
<tr>
<td>F</td>
<td>100</td>
<td>82</td>
<td>82</td>
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<tr>
<td>G</td>
<td>100</td>
<td>89</td>
<td>89</td>
</tr>
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</table>

After correction for recovery of internal standard.

Table III. Reproducibility of TCDD Determination

<table>
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<tr>
<th>sample</th>
<th>internal standard recovery, %</th>
<th>measured, ppt</th>
<th>after correction for recovery, ppt</th>
</tr>
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<tbody>
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<td>39</td>
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<tr>
<td>7</td>
<td>88</td>
<td>48</td>
<td>55</td>
</tr>
</tbody>
</table>

rel. stand. dev., % 17 21 11
response at m/e 320 while the bottom trace represents the sum of responses at m/e 320, 322, 324, 332. The chromatograms are at equal sensitivities for the two samples. In the left-hand chromatogram the large peak at m/e 320 retention time ~3.5 min is DDE. The broad peak has been proposed to be high molecular weight alcohols based on GC-MS analysis. Most of the peaks observed in the lower trace are due to PCBs. In the right-hand chromatogram a small peak at the TCDD retention time is observed in the lower trace. This is due to the internal standard, 13C-TCDD, added to the sample (500 ppt) before the sample preparation. Clearly, in this instance using a low-resolution, quadrupole gas chromatograph–mass spectrometer, there is a dramatic improvement in the level of interferences observed by GC-MS.

Two method modifications have been studied to provide increased sensitivity or selectivity in the clean-up procedure. First, the sample weight has been increased from 10 to 40 g to determine the effect on clean-up efficiency. Second, another reactant column containing alkaline potassium permanganate on silica was used to further remove interferences, presumably of biological origin, from sample extracts.

The effect of increased sample size is shown in Figure 3. The left-hand traces show the mass chromatograms obtained from the analysis of the extract of 40 g of control trout concentrated to 20 μL. The right-hand chromatograms were obtained from the extract of 10 g of the same fish concentrated to 20 μL. The 13C-TCDD internal standard was added to each sample at the same concentration level, 500 ppt. The 10-g sample contained 5 ng of 13C-TCDD and the 40-g sample contained 20 ng of 13C-TCDD. The peak eluting slightly later than TCDD at m/e 320 is a phthalate which was found in one of the reagents. From the full-scale factors on the GC-MS chromatograms one can see that a fourfold increase in sample size has resulted in an increase of only 1.5 times in the amount of background response. Detection limits decreased by about a factor of two for the larger sample size. Thus, a definite advantage can be gained by increasing sample size and concentration factor, but not in direct proportion to sample size.

The use of alkaline potassium permanganate for the oxidation of potential interferences was also examined. This reagent column (1 × 10 cm) containing 4.0 g of adsorbent was
Figure 3. Effect of sample size on clean-up efficiency. Control trout, cleaned-up as described in this work. (A) 40 g flesh, concentrated to 20-μL final volume. TCDD LoD = 8 ppt. (b) 10 g flesh, concentrated to 20-μL final volume. TCDD LoD = 15 ppt.

added to the first column system between the H₂SO₄/silica and the "solvent exchange" columns. The hexane eluent from the H₂SO₄/silica was run directly through the KMnO₄/silica and onto the "solvent exchanger". Recovery of TCDD from the KMnO₄/silica was 99%. In some cases such as for the removal of alkylbenzenes, aldehydes, or alkenes, this alkaline oxidation can be very useful. It was not used for all of the samples because its benefit was not evident in all cases.

The analytical method described for the determination of TCDD in fish provides excellent removal of potential interferences such as DDE, PCB, and chlorobenzylphenyl ethers by a variety of liquid chromatographic steps. In some cases the removal efficiency has been determined for a given step in the procedure. The high efficiency basic alumina column removed approximately 99.8% of PCBs from a trout extract. A similar experiment with the ODS HPLC step showed removal of ~99.5% of PCBs relative to TCDD. Thus, these two steps in series will provide removal of 99.999% of PCBs present in the original sample. A fish containing 1 ppm PCB residue can be analyzed for TCDD at the 10-ppt level even if no PCBs are removed in other steps.

Greater removal efficiencies are expected for DDE. Although the AgNO₃/silica column is intended to be a trap for DDE residues, the removal efficiency has been determined only for the coupled two-column system of AgNO₃/silica and the high efficiency basic alumina. In this case 99.97% of DDE was removed from a fish extract. The ODS column which was designed to be a polishing step (getting improved efficiency when smaller amounts of residue are placed on the column) has eliminated 99.9% of the DDE from a fish extract that was not purified on the AgNO₃/silica column. Combined, the AgNO₃/silica, basic alumina, and ODS columns should be capable of removing a >2 × 10⁶ excess of DDE over TCDD content. Thus, for a 10-ppt determination of TCDD, no interference problems should be encountered for samples containing as much as 20 ppm DDE.

Co-workers have recently reported (13) the identity of a group of compounds, chlorinated benzylphenyl ethers, which can be direct interferences in the determination of chlorinated dibenzo-p-dioxins.

Although a removal calculation has not been made for the elimination of chlorinated benzylphenyl ethers on the HPLC column, a standard of 2,6-dichlorobenzyl-2,4,5-trichlorophenyl ether (26B245PE) elutes significantly before the TCDD zone (relative retention time 0.63 with TCDD 1.00) so that a high separation efficiency is expected. A standard of 2,6-dichlorobenzyl-2,4,5-trichlorophenyl ether was analyzed by GC-MS under the same conditions used for TCDD analysis. The results of that experiment were: (1) 26B245PE elutes at virtually the same retention time as TCDD on the packed GC column. (A glass 28-m WCOT Dexsil 300 capillary will provide some separation.) (2) The 13C isotope of the M⁻Cl⁺ ion gives responses at m/e 320, 322, and 324 with a four chlorine isotope ratio. The 26B245PE response at m/e 320, 322, 324 is about 1/160 of the TCDD response. Thus 1.5 ppb of 26B245PE in the final extract will give the same response as approximately 10 ppt TCDD if the HPLC cleanup is not used.

In addition to the above method using these clean-up procedures and measurement of TCDD by GC-MS using a low resolution spectrometer, additional specificity can be obtained when ion-monitoring is done with higher mass spectral resolution (resolution 1000). When the cleaned-up extract of control trout flesh spiked with 10 ppt TCDD were
examined in this manner, lower limits of detection were obtained due to the mass separation of the hydrocarbon background (with its much larger positive mass defect) in the presence of TCDD. Table IV shows the results obtained. As can be seen, 10-ppt concentrations (0.1-ng amounts) of TCDD are carried through this procedure with very good efficiency.

As has been described by Buser (16), the use of GC-MS can provide a high degree of specificity and sensitivity in the determination of TCDD in environmental samples. For matrices with a high lipid content or those containing large excess amounts of other chlorinated aromatic compounds, considerable cleanup is generally required to achieve low detection limits. Although capillary column GLC can provide good resolution, this LC cleanup followed by packed column GC is an alternate method for both high sensitivity and selectivity.

ACKNOWLEDGMENT

The authors acknowledge the support and advice of Warren Crummett, Nels Mahle, Curt Pfeiffer, and William Parker in the development and accomplishment of this work.

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Surface Acoustic Wave Probe for Chemical Analysis. I. Introduction and Instrument Description

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Chemistry Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Surface acoustic waves are easily propagated along a quartz or lithium niobate surface. Interdigitized finger transducers serve as transmitters of 30–60 MHz SAW waves toward an equivalent detector. Surface molecules predictably affect the wave propagation. Circuity has been built to measure such interactions by changes in amplitude or phase-angle shift of the SAW, or the alteration of the resonance frequency when the device is part of a “tank” circuit. Amplitude response is proportional to the pressure of gaseous molecules in the environment. For a given gas, the response factor is proportional to (molecular weight)\(^{1/2}\). Large linear frequency shifts were noted as ambient pressures changed. Amplitude measurements on quartz have the best S/N ratio (566). Limited data suggest that LiNbO\(_3\) devices have considerably better S/N ratios.

Modern instrumentation systems require a transducer to convert the physical property of interest into a form which is ultimately sensible to the scientist. The major advances in instrumentation art have been invariably preceded by major advances in the transducer art. This article describes the research and development of a new type of transducer: the Surface Acoustic Wave (SAW) Device.

The principle of operation of this transducer is conceptually quite simple. An acoustic wave confined to the surface of some substrate material is generated and allowed to propagate. If matter is present on the same surface then the wave and the matter will interact in such a way as to alter the properties of the wave (e.g., amplitude, phase, harmonic content, etc). The measurement of changes in the surface wave characteristics is a sensitive indicator of the properties of the material present on the surface of the device.

The convenient generation of a surface acoustic wave requires a substrate material which is piezoelectric. Applying a time varying electric field to the piezoelectric material will cause a synchronous mechanical deformation of the substrate with a coincident generation of an acoustic wave in the material. Proper selection of a single crystal orientation for the substrate will result in the acoustic wave propagation being constrained to the surface. While the generation of a number of different types of surface acoustic waves are possible (17), this research utilized only Rayleigh wave propagation. The

\(\text{TCDD,} ^{a}\) ppt

| sample | added | found | recovery, \%
<table>
<thead>
<tr>
<th></th>
<th></th>
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<tr>
<td>C</td>
<td>10</td>
<td>7</td>
<td>70</td>
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Mean of 100 rel. stand. dev., \% 21

\(^{a}\) Results obtained at resolution 1000 on AEI MS-30. Results have been corrected for internal standard recovery.

Ref.


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