

Figure 3. Mass spectra of 1,3-dichloropropene, 1,2-dibromoethane, and 1,2-dibromo-3-chloropropane. Ionization voltage was 66 eV.

interfered with the determination of DCP and EDB. Acetonitrile produced the best recoveries and the lowest background. As shown in Figure 1, a component with retention time slightly less than that of EDB occurred in extracts of all commodities at a level equivalent to approximately 7 ppb of EDB. No interfering compounds were present during the analysis of DBCP as shown in Figure 2. The minimum detectable amount of each compound was estimated to be 3 ppb for *cis*- or *trans*-DCP, 14 ppb for EDB, and 0.3 ppb for DBCP using a 2:1 signal:noise ratio.

Mean recoveries of fumigant added to various commodities were constant over a 100-fold range of concentration as indicated by the data in Table II. A salt concentration of at least 5 M was required to obtain satisfactory recoveries of DCP when partitioning into hexane. Lower concentrations did not affect the recovery of EDB or DBCP.

Confirmation of fumigant residues was carried out by GLC-mass spectrometry. As shown by the spectra in Figure 3, none of the compounds gave a molecular ion in sufficient abundance to be useful for detection by single ion monitoring. Using the stated fragment ions, and with a 2:1 signal:noise ratio, a lower limit of detection of 0.050 ppm for DCP and 0.025 ppm for EDB and DBCP was established with vegetable extracts.

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LITERATURE CITED

- Beckman, H., Bevenue, A., *J. Agric. Food Chem.* **11**, 479 (1963).
 Berck, B., *J. Agric. Food Chem.* **22**, 977 (1974).
 Heuser, S. G., Scudamore, K. A., *J. Sci. Food Agric.* **20**, 556 (1969).
 Karasz, A. B., Gantenbein, W. M., *J. Agric. Food Chem.* **19**, 1270 (1971).
 Malone, B., *J. Assoc. Off. Anal. Chem.* **53**, 742 (1970).

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X-Ray Fluorescence Spectroscopic Determination of Br⁻ Residues in Crops after Soil Treatment by Methyl Bromide

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Dried samples of lettuce, pepper, and cucumber cultures, grown on soils treated with CH₃Br and on nontreated soils, have been analyzed for their Br⁻ content by x-ray fluorescence spectroscopy (XRFS). Variations in the Br⁻ concentrations in the plants have been followed during a growing period of several months. It appears that the levels for the treated soils considerably exceed at all times the maximum values admitted in most European countries and seem to be approximately inversely proportional to the total dry weight material of the crops. The x-ray fluorescent (dispersion) spectroscopic technique, used here, reveals to be perfectly adapted for analysis in this concentration range and may be used as a very rapid screening technique for the detection of bromine in crop material. In order to obtain some information about the accuracy of the technique, the results obtained by this technique have been compared with those obtained by a colorimetric method for a number of cases.

Intensive crop cultures require a careful control of the soil conditions. Furthermore, to obtain good yields in those cultures it is necessary to eliminate harmful effects of weeds and mold as much as possible. Therefore, the

treatment with pesticides, fungicides, and soil disinfectants is practically unavoidable. Their use, however, gives rise to new problems, such as those related to the presence of their residues in the plant.

Among the many soil disinfectants CH₃Br takes an important place because of its efficiency against mold and weeds. After application this CH₃Br is rapidly converted to inorganic bromide in the soil and can be accumulated

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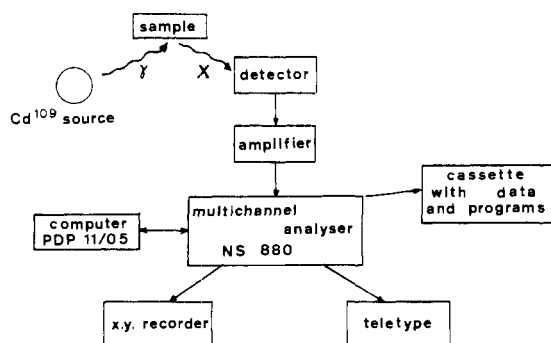


Figure 1. Block diagram of XRFS instrumentation.

by the plant in that form. Apart from the aspect of public health related to the presence of the bromide, it can also cause phytotoxic action. For assessing the soil and plant contamination by bromide, two methods of analysis have generally been used. A method based on "neutron activation analysis" has been described by Guinn and Potter (1962), Castro and Schmidt (1962), and Stärk et al. (1971). A colorimetric procedure has been developed by Drosihn (1967) and Malkomes (1970) and is based on calcination of the plant material and oxidation of bromide to hypobromite, which reacts, in a buffered medium, with phenol red to tetrabromophenol blue. However, both of these methods suffer from certain disadvantages. The first method requires a very special and costly instrumentation, while the second is cumbersome and time consuming.

In this work it was our purpose to evaluate the possibilities of a technique which is rapid, reduces manipulations to a minimum, and is easily adaptable for automatization. Such a promising technique reveals to be x-ray fluorescence spectroscopy (XRFS).

Although the diffraction technique is the more common and has already been applied for determination of bromine residues (Getzendaner et al., 1968), the energy dispersion XRFS offers, in turn, great possibilities because of simplicity and simultaneous multi-element determination. This latter has been applied here for bromide analysis in peppers and cucumbers during their growing time. These crops have been grown on soils treated with CH₃Br as well as on nontreated soils. Furthermore, a comparison of the results obtained by this technique and the colorimetric method has been made for a number of samples, giving some data on the validity of the method.

INSTRUMENTATION AND EXPERIMENTAL SECTION

Apparatus. The block scheme of the principle of the XRFS technique and the instrumentation is given in Figure 1. The prepared sample is excited by the γ rays of a ¹⁰⁹Cd source and produces K and L x-rays with energies characteristic of the elements that are present. These x-rays are detected with a Si(Li) semiconductor detector. After pulse conversion and amplification, they are analyzed with a multichannel analyzer which is energy discriminating. The multichannel analyzer is connected with a cathode ray tube, where the obtained spectrum is displayed, a cassette storing the programs and data, a 8K computer, an X-Y recorder, and a teletype, permitting the plotting of the spectra.

Sample and Standard Preparation. Plant material and soils are first dried at 130 °C during 12 h in a vacuum dessicator and grinded afterwards to a fine powder. The homogenized powder is directly pressed to a pastille in a x-ray Die, DX-04, Beckmann at a constant pressure of 25 tons/cm². Apart from bromide there are also traces of Fe, Zn, K, Ca, and Cu..., which cause x- and γ -ray selfabsorption of the matrix. To eliminate differences in ab-

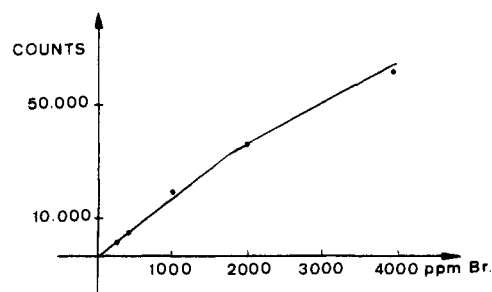


Figure 2. Standard curve for lettuce.

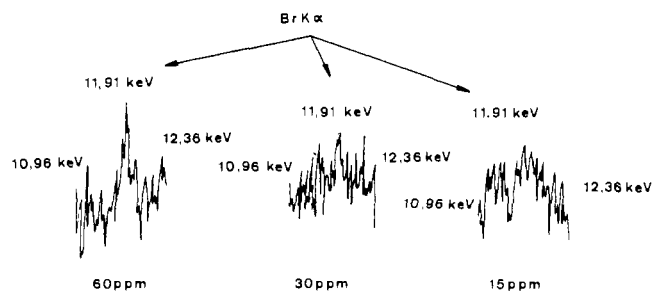


Figure 3. Net spectra of Br⁻ diluted in a Li₂CO₃ matrix for detection limit determination.

sorption of the matrices due to these elements, standards have been made starting from bromide-free plant material (lettuce, cucumber, or pepper) which also served as blank. A known quantity of LiBr has been added to this, and a series of standards is then set up by successive dilution with blank plant material.

Calibration Curve. To define the calibration curve, a computer program has been developed which uses background subtraction of the standard blank and subsequent peak integration of the K _{α} rays of bromium.

A typical standard curve for lettuce, obtained by using this technique is given in Figure 2. As can be seen from Figure 2, this calibration curve is reasonably linear up to at least 1000 ppm. The calibration curves for the other crops are superposed on this curve. For determining the detection limit of the method, however, standards of LiBr have been diluted with Li₂CO₃. In this way net spectra of the bromide x-rays have been obtained, while x-ray fluorescence signals due to Li cannot be observed by this technique. In Figure 3 the curves in the K _{α} peak region of Br (from 10.96 to 12.36 keV) have been plotted for three standards of very low content. They have been measured in the same experimental conditions as those used for the plant analysis (same counting time and geometry). From this, a detection limit of about 30 to 40 ppm may be visually derived. The exact calculation of this limit, based on statistical methods did not prove necessary for our purpose.

Analysis of Pepper and Cucumber Cultures. Pepper and cucumber cultures have been grown in greenhouses on soils fumigated with CH₃Br about 6 weeks before seeding time and on nontreated soils. The fumigation doses was 9.5 kg CH₃Br/acre. Samples of these crops and from the soils have been taken at regular intervals for subsequent analysis. Thus it was possible to investigate the rate of absorption and the variation in bromide content of the plants as a function of time. The results of the analysis on cucumber and pepper cultures are given in Tables I and II, respectively. In order to check the validity of the used method, a number of samples has been analyzed for both XRFS and colorimetry, to evaluate the agreement that exists between these two methods. The colorimetric results have been obtained following the

Table I. Results of the Cucumber Culture

| Time (in days, after CH ₃ Br treatment) | Sample | Percentage of dry mat. (dry weight) | Br ⁻ content in ppm | |
|--|----------------|-------------------------------------|--------------------------------|------------|
| | | | Dry mat. | Plant mat. |
| 40 | b | | | |
| 50 | C ^a | 3.2 | < 30 | < 1 |
| | C | 3.4 | 3500 | 119 |
| | S ^a | | < 30 | |
| 60 | S | | 50 | |
| | C ^a | 4.2 | 30 | 1 |
| | C | 3.1 | 2380 | 74 |
| 65 | S ^a | | < 30 | |
| | S | | 40 | |
| | C ^a | 3.3 | 30 | 1 |
| 70 | C | 3.5 | 2340 | 82 |
| | S ^a | | < 30 | |
| | S | | 40 | |
| 80 | C ^a | 2.9 | 30 | 1 |
| | C | 2.5 | 2420 | 60 |
| | S ^a | | < 30 | |
| 80 | S | | 60 | |
| | C ^a | 3.7 | 30 | 1 |
| | C | 2.7 | 2120 | 57 |
| | S ^a | | < 30 | |
| | S | | 70 | |

^a Untreated samples; C = cucumber; S = soil sample.

^b Planting of the cucumbers.

Table II. Results of the Pepper Culture

| Time (in days, after CH ₃ Br treatment) | Sample | Percentage of dry mat. (dry weight) | Br ⁻ content in ppm | |
|--|----------------|-------------------------------------|--------------------------------|------------|
| | | | Dry mat. | Plant mat. |
| 55 | b | | | |
| 130 | P ^a | 6.3 | 30 | 2 |
| | P | 6.8 | 1450 | 99 |
| | S ^a | | < 30 | |
| 140 | S | | < 30 | |
| | P ^a | 7.5 | 30 | 2 |
| | P | 6.0 | 980 | 59 |
| 180 | S ^a | | < 30 | |
| | S | | < 30 | |
| | P ^a | 6.2 | 30 | 2 |
| 190 | P | 5.9 | 810 | 48 |
| | S ^a | | < 30 | |
| | S | | < 30 | |
| 190 | P ^a | 6.2 | 70 | 4 |
| | P | 6.2 | 640 | 40 |
| | S ^a | | < 30 | |
| | S | | < 30 | |

^a Untreated samples; P = peppers; S = soil sample.

^b Planting of the peppers.

method as described by Drosihn (1967). Table III gives the comparative figures obtained for lettuce and cucumber. Although somewhat lower results seem to be obtained by XRFS, one may conclude that there is an acceptable agreement between the two methods, differences probably falling within the error limits.

DISCUSSION OF THE RESULTS

The results on the pepper and cucumber material clearly show that considerable amounts of bromide may be found in cultures grown on CH₃Br-treated greenhouses. In this case, concentrations ranging between 40 and 120 ppm in the plant material itself have been observed (Kempton and Maw, 1972; Wagner, 1969), while the bromide content of

Table III. Comparison Test XRFS Colorimetry

| Sample number | Concentration of Br ⁻ (ppm dry material) | |
|---------------|---|-------------|
| | XRFS | Colorimetry |
| A. Lettuce | | |
| 1 | 2100 | 2580 |
| 2 | 5300 | 5650 |
| 3 | 6000 | 6700 |
| 4 | 1760 | 1950 |
| 5 | 2700 | 3100 |
| B. Cucumber | | |
| 1 | 3500 | 4160 |
| 2 | 2340 | 2490 |
| 3 | 2380 | 2930 |
| 4 | 2120 | 1730 |
| 5 | 2420 | 2290 |

the nontreated plants is much lower (a few ppm only), and are near the detection limit of the XRFS method. Thus, these latter concentrations are only raw estimations of the natural content. They are nevertheless of the same order of magnitude as those found by Van Wambeke (1974) and by Van Wambeke et al. (1974) for untreated plant material in Belgium.

Furthermore, it is very obvious that there is a constant decrease in the bromide content for both cultures as sampling time after treatment becomes longer. This goes, however, together with the growing of the crops. One may thus conclude that a considerable quantity of bromide is taken up by the plants at an early stage and that the decrease is mainly attributable to further plant development where no uptake takes place any longer.

As can be seen, the decrease is not always very regular. However, at each time differing sets of samples were used for analysis (three to four plants per set) and thus a certain Br⁻ variation per set should be taken into account.

As for the soil samples, it was very difficult to reveal whether residues of bromide persisted in the treated soils or not with this technique. Some evidence has been found for this, but the interpretation is compromised by the fact that untreated and treated soils showed contents that were too near the detection limit of the method.

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LITERATURE CITED

- Castro, C. E., Schmidt, R. A., *J. Agric. Food Chem.* **10**, 236-239 (1962).
 Drosihn, U. G., Thesis, Hannover, 1967.
 Getzendaner, M. E., et al., *J. Agric. Food Chem.* **16**, 265-271 (1968).
 Guinn, V. P., Potter, J. C., *J. Agric. Food Chem.* **10**, 232-236 (1962).
 Kempton, R. J., Maw, G. A., *Ann. Appl. Biol.* **72**, 71-79 (1972).
 Malkomes, H. P., Thesis, Hannover, 1970.
 Stärk, H., et al., *Landwirtsch. Forsch.* **24**, 133-201 (1971).
 Van Wambeke, E., *Agric. Environ.* **1**, 277-282 (1974).
 Van Wambeke, E., et al., *Med. Fak. Landb. Gent.* **39**(2), 1311-1324 (1974).
 Wagner, F., *Gesunde Pflanz.* **22**, 138 (1969).

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