A SIMPLE METHOD IS DESCRIBED FOR THE FIELD DETECTION OF MERCURY IN POLLUTED WATER, AIR AND SOIL SAMPLES.

SUMMARY

A simple method is described for the field detection of mercury. The method is based on the ligand exchange reaction where hexacyanoferrate (III) exchanges its cyanide ions with chromogenic organic ligand succinylidyldihydroxamic acid (SDHA). In the reaction, the colourless SDHA reacts with yellow $K_2 Fe(CN)_6$ to give a greenish blue coloured complex in a slightly acidic solution containing mercury, showing maximum absorption at 700 nm. The reaction has been successfully applied for the detection of mercury in polluted water, air and soil samples. In air, at a velocity of $\sim 0.2$ l/min of the impinging air and a reaction temperature of $\sim 70^\circ$C, mercury (II) as low as 0.01 µg could be easily detected after 3 minutes exposure. In water, the limit of identification and limit of dilution were found to be 0.2 µg Hg (II) and 1:2,00,000 respectively.

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A NOVEL FIELD TEST FOR THE DETECTION OF MERCURY IN POLLUTED WATER, AIR AND SOIL SAMPLES

Mercury is one of the most hazardous environmental pollutants and is therefore a substance of first order priority in ecotoxicology (1). The largest present use of mercury is in electric industries for production of relays, switches, batteries, rectifiers and lamps. Mercury and its compounds are also widely used in cellulose industries for preserving the wet pulp from biodeterioration, plastic industries for catalytic reactions, pharmaceutical industries for production of diuretics, antiseptics, cathartics, some contraceptives and drugs for treatment of congestive heart failure, paint industries for production of anticorrosive paints, in plants treating nuclear wastes for electrolytic purification of wastes, industries producing industrial and control instruments such as thermometers, barometers and mercury pumps and as catalysts for amalgamation (2,3). Recent survey reveals that mercury is also found in canned sea foods (4).

Mercury and its salts are recognized as general cellular poisons and effective protein precipitants because of their release of $\text{Hg}^{2+}$ ion (3). It came into lime light after the incidence of "Minamata disease" in 1953 in Japan. The disease is associated with the ingestion of fish collected from mercury polluted waters. The main symptoms of the disease is "central nervous system disorder" which leads to numbness of lips and
limbs, impairment of vision, hearing and speech and difficulty in walking and performing simple manipulations (5). The toxicity of mercury depends on its chemical species and it is found that organomercurials are highly toxic compared to inorganic mercury compounds (6). Mercury and its compounds are reported to be mutagenic and teratogenic in nature (7,8). Mercury chloride when inhaled by female mice on the days of pregnancy retarded the development of bone in the embryos. In addition, the number of embryo cells with chromosomal aberrations also increase considerably (7). Mercury is a health hazard because of the strong bonds formed by it with sulphur atoms in the body. This formation interferes with the functions and the synthesis of both enzymes and proteins (9). The most important routes of mercury and its compounds into living system are via the lungs and absorption through the skin. After absorption, it circulates in the blood and gets stored in the liver, kidney, spleen and bone (5,10). Acute intoxication leads to cystinuria and pharyngitis and chronic toxicity is accompanied by muscular tremors and psychic disturbances (3,5,8). Mercury is propagated in the food chain in the following pattern (6).
The threshold limit value for mercury is reported to be 0.1 mg/m$^3$ (0.01 ppm) by ACGIH (3). Apparently the maximum non-toxic level of mercuric chloride exposure is 0.005 mg/l/day and 0.003 mg/m$^3$ mercuric chloride in air (11).

Owing to the toxicity of mercury in the environment, the determination of trace amounts of mercury has attracted great attention. The conventional technique of dithizone extraction (12-14) is not always favoured because the procedure is cumbersome, sensitive to light and is subject to interferences from other metal ions. Analytical methods based on ternary complex formation seems to offer superior sensitivity and selectivity (15,16). However, most of the ternary system involve an additional extraction step. Colour development and measurement in aqueous solution itself would alleviate this difficulty. Mateo and Lacort (17) have reviewed the methods for the determination of mercury. Some of the chromogenic reagents used
for the determination of mercury are 4(2-pyridyl azo)
resorcinol (18), trimethylammoniophenyl porphine (19),
diethyldithiocarbamate (20), rhodamine 6G (21), 2,2'-
bipyridyl bis (2-quinolyl hydrazone) (22), 1,10-phenan-
throline (23) and others (24-30). Although most of these
methods have a remarkable sensitivity, their selectivity
is sometimes low and this leads to the development of a
rapid, more accurate and precise analytical method. Only
a few systems have been reported which involve ligand-
exchange reactions (31-38) and these methods are simple
and sensitive for the determination of mercury. In the
present investigation also a similar method has been
developed for the detection of mercury.

Apart from colorimetric methods some of the
instrumental methods reported for the estimation of mercury
are atomic absorption spectrophotometry (39,40), high
potential liquid chromatography (41), photoacoustic spectrom-
metry (42), neutron activation analysis (43), mass spectrom-
metry (44), fluorimetry (45), ion chromatography (46) and
liquid chromatography (47).

In the present text a simple field test for detection
of mercury has been developed based on the ligand-
exchange reaction, where hexacyanoferrate (III) exchanges
its cyanide ions with chromogenic organic ligand, succi-
nyldihydroxamic acid (SDHA). In the reaction the colour-
less SDHA reacts with yellow $K_2Fe(CN)_6$ to give a greenish-
blue coloured complex in a slightly acidic solution
containing mercury. Due to auto-catalytic reaction of mercury it takes 24-30 hours for the complete colour development, therefore a reliable quantitative determination of mercury could not be achieved in a short time. Due to various critical parameters as reported earlier (32-34) such as time, temperature, quenching process, etc. in the present investigation the reaction could not be used for the quantitative determination of mercury. But the method can easily be applied for the detection of mercury in water, air and soil samples.

**EXPERIMENTAL**

**APPARATUS** - Midget impingers of 35 ml capacity, a vacuum pump, spot plates and micro test tubes were used for the detection of mercury in air and soil samples.

**REAGENTS** -

Stock mercury solution - 1 mg/ml solution was prepared by dissolving 135.36 mg mercuric chloride in 100 ml of demineralised water. Working standards were prepared by appropriate dilution of the stock.

Hexacyanoferrate III \( K_3[Fe(CN)_6] \) - 1% aqueous solution.

Succinylidihydroxamic acid (SDHA)(48) - Prepared by drop-wise addition of 17.2 g of diethylsuccinate to the ammoniacal solution of 13 g of hydroxylamine hydrochloride with vigorous stirring at 0°C. The white precipitate of SDHA obtained was filtered and crystallized twice with demineralised water (K.P. - 164 - 166°C). The compound is stable for long periods.
0.1% aqueous solution was used as reagent.

Metallic mercury - AnalaR grade.

PROCEDURE -

A. Spot test for the detection of mercury:

A drop of the test solution was placed on a spot plate or in a microtest tube. To it one drop of hexacyanoferrate (III) was added followed by one drop of SDHA. The mixture was warmed in an oven at ~70°C for 10 minutes. A greenish blue colour appeared on the plate and test tube indicating the presence of mercury. For very small amounts of mercury a blank test was also preferred.

B. Detection of mercury in air:

An impinger containing a known aliquot of mercury as mercury chloride was connected to another impinger with the reagent solution containing equal volumes of 1% K₃Fe(CN)₆ and 0.1% SDHA. These two impingers were then connected to a source of suction. When lower concentrations of mercury are dealt with heating accelerated the reaction, hence the impinger containing reagent solution was kept in a water bath (~70°C). Mercury was released from mercuric chloride by the addition of excess of stannous chloride. Air was drawn through impingers at a
rate of ~0.2 l/min for 3 minutes. The presence of mercury was indicated by the change of yellow colour of test solution in the second impinger to greenish blue.

APPLICATION OF THE METHOD

In polluted water – Water samples drained from fields sprayed with mercurials used as fungicides were collected and filtered prior to analysis. The samples were then analysed as described in procedure A.

In soil – The soil samples sprayed with mercurials were collected for the detection of mercury. The samples were washed thoroughly with two 5 ml portions of ethanol and filtered. The filtrate was then analysed as recommended in procedure A.

In air – 2-3 globules of metallic mercury were taken into an impinger and connected to another impinger kept on a water bath (~ 70°C) containing test solution. Both the impingers were then connected to a source of suction and mercury was analysed as described in procedure B.

In all the above cases the colour of test solution turned from yellow to greenish blue indicating the presence of mercury in these samples.
RESULTS AND DISCUSSION

The method is simple and is based on the ligand exchange reaction. SDHA reacts with yellow $KFe(CN)_6$ at pH 3 - 5.5 to give a greenish blue solution in presence of mercury (II) ion. No colour change was observed when mercury was added independently to $KFe(CN)_6$ or SDHA solutions, proving that the colour formation between $KFe(CN)_6$ and SDHA is due to the ligand exchange reaction in presence of mercury (II).

The reaction was also carried out with hexacyanate(II) and sodium nitroferricyanide dihydrate, but was found to be less sensitive.

Reaction mechanism - The reaction of hexacyanoferrate(II) with an organic ligand in presence of mercury is reported to take place in the following manner (33):

$$Fe(CN)_6^{4-} + H_2O \rightarrow Fe(CN)_5.H_2O^{3-} + CN^- \quad \text{(1)}$$

Slow

$$[Fe(CN)_5.H_2O]^{3-} + L \rightarrow [Fe(CN)_5.L] + H_2O \quad \text{(2)}$$

Organic ligand

$$CN^- + H_2O \rightarrow HCN + OH^- \quad \text{(3)}$$

Mercury catalyses the decomposition of hexacyanoferrate in the following manner -

$$Hg^{2+} + [Fe(CN)_6]^{4-} \rightarrow HgCN + [Fe(CN)_5.H_2O]^{3-} + HgCN \quad \text{(4)}$$

$$HgCN + H^+ \rightarrow Hg^{2+} + HCN \quad \text{(5)}$$
The aquopentacyanoferrate (III) reacts with organic ligands to produce coloured products. In the proposed method it is likely to show similar reaction using hexacyanoferrate (III) and an organic ligand SIDHA in presence of mercury liberated from mercuric chloride to give greenish blue colour for the detection of mercury.

**Effect of pH** - It was observed that the maximum colour of the complex was obtained in the pH range of 3 - 6. The intensity of colour decreased at lower pH, whereas no colour was obtained at higher pH. However, it was found that the reagents used as test solution themselves produced pH ~ 5.5, which was sufficient for the colour development.

**Effect of time and temperature** - The effect of time and temperature for the reaction is reported to be critical (32-34). We observed that at thermostated temperatures ranging from 20 - 50°C it took 30 - 60 minutes for the initiation of colour development, whereas at 70 - 90° it took only 5 minutes for colour development. It was also observed that longer heating time caused decomposition of the greenish blue complex and an increased blank, hence the experiment was carried out in a water bath at 70°C for 2 - 10 minutes.
CONCLUSION

The present method was compared with various other reported colorimetric spot test methods and was found to be of comparable sensitivity (12, 38, 49) (Table - I). The method was found to be free from interference of various metal ions and ions like nitrate, chloride and phosphate. Pesticides other than organomercurials like carbamates, organochlorine, organophosphorus pesticides, etc. also do not interfere with this reaction. Silver (I) and palladium (II) give analogous reaction. Iron (II) and iron (III) ions interfere due to the formation of coloured precipitate. The greenish blue coloured complex formed in presence of mercury was stable for more than a week.


### TABLE - I

**COMPARISON WITH SOME REPORTED SPOT TEST METHODS (12, 38, 49)**

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Test for</th>
<th>Details of method</th>
<th>Result</th>
<th>I.L. (^a)</th>
<th>D.L. (^b)</th>
<th>Principal Interferences</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Diphenyl carbazone</td>
<td>Hg(I) or Hg(II)</td>
<td>0.2M HNO(_3); on paper</td>
<td>Blue to violet spot</td>
<td>1.0</td>
<td>5x10(^4)</td>
<td>Cr(IV), Mo(IV), Au; V(V) and Fe(III)</td>
</tr>
<tr>
<td>2. Dithizone</td>
<td>Hg(I) or Hg(II)</td>
<td>0.5M HNO(_3), Hg concn. must be very low; extract into CCl(_4) phase</td>
<td>Yellow Hg(I), Orange Hg(II) colour in CCl(_4) phase</td>
<td>0.25</td>
<td>1.1x10(^5)</td>
<td>Several metals particularly Cu, Ag, Au, Bi, Pd.</td>
</tr>
<tr>
<td>3. P-dimethylaminobenzylidenehydridane</td>
<td>Hg(II)</td>
<td>Weakly acidic (pH &gt; 1) add 3 drops satd. NaAc if Cl(^-) is present on spot plate</td>
<td>Reddish violet suspension or precipitate</td>
<td>0.33</td>
<td>1.5x10(^5)</td>
<td>Ag in particular also Au, Cu(I), Pt and Pd.</td>
</tr>
<tr>
<td>4. Ferrocyanide ion + (\alpha\alpha) dipyridyl</td>
<td>Hg(II)</td>
<td>Heat 1 drop each of K(_4)Fe(CN)(_6), NH(_3) and (\alpha\alpha) dipyridyl in micro test tube Fe(^{2+}) liberated.</td>
<td>Pink to red colour at once or within few minutes</td>
<td>2</td>
<td>2.5x10(^4)</td>
<td>Ag and Pd(II) give analogous reactions.</td>
</tr>
<tr>
<td>5. Ferrocyanide ion + SDHA (Present method)</td>
<td>Hg(II)</td>
<td>Heat 1 drop each of K(_2)Fe(CN)(_6) and SDHA in micro test tube or on a spot plate.</td>
<td>Green to blue colour at once or within few minutes</td>
<td>0.2</td>
<td>2x10(^5)</td>
<td>Ag and Pd(II) give analogous reactions most of the metal ions do not interfere.</td>
</tr>
</tbody>
</table>

\(a\) - Identification limit in \(\gamma\) of Hg;  
\(b\) - Dilution limit.
REFERENCES


