Application of energy dispersive X-ray fluoresce spectrometry (EDX) in medico-legal autopsy case


Publicado por: Imprensa da Universidade de Coimbra; International Academy of Legal Medicine

URL persistente: URI:http://hdl.handle.net/10316.2/31854

DOI: DOI:http://dx.doi.org/10.14195/978-989-26-0173-1_55

Accessed: 24-Mar-2021 22:02:51


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APPLICATION OF ENERGY DISPERSIVE X-RAY FLUORESCE SPECTROMETRY (EDX) IN MEDICO-LEGAL AUTOPSY CASE

Abstract: We applied here energy dispersive X-ray fluorescence spectrometry (EDX) to medico-legal autopsy case of drowning in a river under the influence of hypnotics. Rapid elemental analysis using EDX identified bromide in blood, urine and cerebrospinal fluid of victim during autopsy. Subsequent toxicological analysis with a high performance liquid chromatography revealed bromovalerylurea in blood and other specimens. Present case shows that screening using EDX, ideal examination for non-destructive, rapid elemental analysis, provides useful information for identification of drugs.

Introduction

Rapid screening for drug overdose and the estimation of toxic substances are important in the fields of both emergency medicine and forensic toxicology. Such screening is usually performed using an immunological screening kit or color test paper [1].

Energy dispersive X-ray fluorescence spectrometry (EDX) is an easy and convenient way to identify various elements without special sample preparation [2]. Therefore, EDX is a quite useful tool for the primary identification of toxic compounds or pharmaceutical drugs including those such as arsenic and bromine.

We previously reported EDX was useful for screening of drugs in medico-legal autopsy cases [3]. Here, we report toxicological screening by EDX in another case of bromovalerylurea ingestion which was not revealed by police investigations.

Case history

A male in his thirties (height 188 cm, weight 115 kg) was found dead in the river below the bridge. He had told to his families about his attempt of suicide. Police investigation revealed that he was suffered from depression but the medications were unclear other than diphenhydramine, commercially available as over-the-counter hypnotics in Japan. The postmortem interval was estimated to be approximately 12 hours.
At autopsy, the lungs (left 550 g and right 370 g in weight) were edematous with marginal emphysema. White frothy fluid was found in the trachea and both bronchi. There was 500 ml of light-brownish stomach contents, and 4 ml of brownish liquid in sphenoidal sinus. Diatom test of lung, liver, kidney and sphenoidal sinus fluid were positive.

A drug screening test of the urine with Triage® (Biosite Diagnostic Inc., CA, USA) panel was positive for barbiturates.

Materials and Methods

The elemental screening tests and the quantification of bromide in blood, urine and cerebrospinal fluid were operated using eDX (JSX3200, JEOL, Tokyo, Japan) [3, 4]. The quantification limit for bromide ion using this method was 19.7 µg/ml.

Toxicological analysis was also performed using a high performance liquid chromatography (HPLC) drug analysis system (Class-VP system, Shimadzu, Kyoto, Japan) [5]. Quantification of ethanol was performed using a head-space gas-chromatography.

Results

EDX spectra of blood, urine and cerebrospinal fluid from victim showed the characteristic lines of bromide (Fig. 1). From the calibration curve, the concentrations of bromide in heart blood, urine and cerebrospinal fluid were calculated as 108.1, 41.2 and 38.0 µg/ml, respectively. Bromide was not detected from the river water using eDX, consistent with our previous report [4].

Subsequent toxicological analysis using HPLC identified bromovalerylurea, barbital and diphenhydramine within the concentrations of toxic levels (Table 1). Concentrations of ethanol in femoral blood and urine were revealed to be 0.08 and 0.22 mg/ml, respectively.

Discussion

From the autopsy findings and the results of diatom test, we determined the cause of death was aspiration of river water under the influence of sedative drugs, including bromovalerylurea.

Bromide concentration in blood from normal healthy subject was reported to be approximately 5.35 µg/ml [6]. We previously suggested that detection of bromide in blood using EDX could be an indicator in cases of drowning in seawater [4]. In present case, bromide was detected from each specimen regardless of freshwater- drowning. These data suggested that he took some chemicals containing bromide before his death. Bromovalerylurea, bromide-containing hypnotics, was identified by the subsequent detailed toxicological examinations using HPLC.
The concentrations of bromide in each specimen detected using EDX were different from those of bromovalerylurea by HPLC, especially in blood and urine. This may be because EDX can detect whole bromide including parent drug and its metabolites, while HPLC can detect only parent drug. Consistent with present case, Maguchi [7] also reported that blood concentration of bromide was higher than that of bromovalerylurea by 6 to 36 times.

It is reported the transfer of bromide ion into cerebrospinal fluid from blood is rarely occurred, whereas, bromovalerylurea easily invades into cerebrospinal fluid without being metabolized to bromide ion in this space [8]. Consistent with this report, in present case the concentration of bromide was more close to that of bromovalerylurea in cerebrospinal fluid than in blood.

EDX has been applied for the detection of some pharmaceuticals or metallic substances in medical fields [3, 9-11]. EDX enables non-destructive, non-degenerative analysis and is useful as a screening test when sample preservation is required for evidence.

Conclusions

We found EDX was useful as primary analysis of drug screening. Further applications in the field of forensic practice can be expected.

References


<table>
<thead>
<tr>
<th>Drug</th>
<th>Heart blood</th>
<th>Femoral blood</th>
<th>Urine</th>
<th>Cerebrospinal fluid</th>
<th>Therapeutic levels in blood</th>
<th>Fatal levels in blood</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barbital</td>
<td>17.7</td>
<td>16.9</td>
<td>62.1</td>
<td>15.0</td>
<td>10-26</td>
<td>more than 100</td>
<td>[12]</td>
</tr>
<tr>
<td>Diphenhydramine</td>
<td>0.9</td>
<td>0.9</td>
<td>5.2</td>
<td>0.4</td>
<td>0.03-0.11</td>
<td>more than 8</td>
<td>[12]</td>
</tr>
<tr>
<td>Bromovalerylurea</td>
<td>9.6</td>
<td>9.1</td>
<td>Not detected</td>
<td>5.2</td>
<td>10-20</td>
<td>44-93</td>
<td>[13]</td>
</tr>
<tr>
<td>Bromide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>more than 3000</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Table 1 – Concentrations of drugs and bromide in each specimen (µg/ml) with their fatal and therapeutic levels.

<table>
<thead>
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Figure 1 – EDX spectra of each sample. The characteristic Kα and Kβ lines of bromide were identified in blood (A), urine (B) and cerebrospinal fluid (C). The concentrations of bromide in blood, urine and cerebrospinal fluid were calculated as 108.1, 41.2 and 38.0 µg/ml, respectively. S-Kα; Kα line of sulfur: K-Kα, β; Kα and Kβ lines of potassium: Fe-Kα, β; Kα and Kβ lines of iron: Br-Kα; Kα line of bromide: Br-Kβ; Kβ line of bromide.