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SIMULTANEOUS DETERMINATION OF CADMIUM AND LEAD IN CIGARETTES AND CIGARETTE SMOKE BY IMPACTION-GRAPHITE FURNACE AND GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

Keywords: impaction, simultaneous, GFAAS, cadmium and lead, cigarette, cigarette smoke

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ABSTRACT

The simultaneous determination of cadmium and lead in cigarette smoke was achieved using a unique impaction-graphite furnace atomic absorption spectrometry system (I-GFAAS), and in inert cigarette parts (whole, tobacco, filter, and paper) using conventional graphite furnace atomic absorption spectrometry (GFAAS) following digestion using a previously established microwave digestion method. Results showed that in both the whole cigarette and the smoke there was about a factor of two in lead compared to cadmium concentrations, typically 17.56 compared to 31.94 mg/g for whole cigarette and 13.41 to 25.72 ng/m³ for cigarette smoke.

*Author to whom correspondence should be addressed, Phone: (318) 478 5781, Fax: (318) 475 5234, E-mail: jsneddon@acc.mcneese.edu. This paper is dedicated to Dr. James W. Robinson, the Editor-in-Chief of Spectroscopy Letters since its inception, on his elevation to Editor Emeritus status.

INTRODUCTION

There are numerous sources of trace metals in human tissue, including diet, and environment. A unique and (considered) toxic source of metals is through smoking cigarettes, both directly as a smoker and indirectly through second-hand smoke. The concentrations of various metals in tobacco products in various countries throughout the world have been determined using neutron activation analysis^{1, 2}, flame atomic absorption spectrometry³⁻⁶, cold vapor atomic absorption spectrometry³ (for mercury), and graphite furnace atomic absorption spectrometry^{7, 8}. For the most part, the determination has been performed on tobacco, ash, filter or paper, despite the fact that it is well known that the smoke from a burning cigarette would be more efficiently carried into the human body.

This work describes the continued use and results of a unique system, based on a single stage impactor and graphite furnace collection surface, for simultaneous graphite furnace absorption spectrometric determination of cadmium and lead in cigarette smoke as well as individual parts of the inert cigarette. The aim was to obtain a comparison between the inert cigarettes and the smoke from a burning cigarette.

EXPERIMENTAL

Instrumentation

A Smith-Hieftje 8000 (Thermo Jarrell Ash-Baird Corporation, Franklin, Massachusetts) atomic absorption spectrometer (AAS) equipped with a CTF 188 controlled temperature atomizer was used. The AAS was used either in the single or simultaneous mode. In the simultaneous mode, up to four elements were determined at a time. The system is described in detail elsewhere^{9, 10}, and uses a galvanometer suspended grating in the monochromator. The galvanometer driven mechanism is used to select hollow cathode lamps, and allows the scanning of the spectrum (190 to 900 nm) in 20 ms. Visimex II hollow cathode lamps and uncoated delayed atomization cuvettes were used.

Cigarette smoke was collected via a single stage impactor onto a graphite tube at a fixed flow rate and time. The graphite tube was removed and inserted into a graphite furnace for atomic absorption

spectrometric determination of cadmium and lead. A detailed description of the laboratory constructed impaction system is described elsewhere^{9, 10}.

Instrumental and Experimental Operating Conditions

All stages of the experimental (drying, pyrolysis, and atomization temperatures and times) and instrumental (hollow cathode lamp current, and slit widths) were optimized and used as described previously⁹⁻¹¹. For simultaneous determination of cadmium and lead, this involved a compromise⁹. It was interesting to note that for the cigarette smoke analysis, a pyrolysis temperature of 400 °C could be used without loss of cadmium, whereas for the digested parts of the cigarette, a pyrolysis temperature of no more than 250 °C could be used before loss of cadmium occurred. The higher pyrolysis temperature used for the cigarette smoke was attributed to the fact that the smoke was acting as a chemical modifier and making the cadmium less volatile.

Materials

Stock solutions of 1000 mg/ml (Fisher Scientific, Pittsburgh, Pennsylvania) were diluted daily or as required with deionized water. Concentrated HCl and HNO₃ were ultrapure chemicals. Standard "Marlboro" 100 type cigarettes were used in the study. When digesting the cigarette parts, particular attention was taken to avoid possible contamination.

Procedure

A laboratory constructed cigarette smoking system was used to generate the cigarette smoke. The cigarette was connected to a tube, which was mounted into the laboratory constructed plexiglass box (dimensions of approximately 60 cm (h) x 45 cm (l) x 30 cm (b)). Following the tube was a flow valve and flow meter. A vacuum pump draws the smoke from the lighted cigarette at a known flow rate into the graphite (impactor) furnace, and the excess leaves the system to be vented into the surroundings. After collection of the smoke at a known time, the system is stopped and the graphite furnace is inserted into the AAS system for determination. With practice, the time from stopping the system and insertion

of the graphite tube into the graphite furnace system was approximately 30 s. The concentration of cadmium and lead in the cigarette smoke was established using aqueous standards and conversion in units of ng/m^3 as described previously⁹. A typical flow rate of 5 L/min for 2.0-3.0 s was used to collect the cigarette smoke onto the impactor.

The determination of the metals was also performed on whole cigarettes, filter, paper, and tobacco.

Concentration units of mg/g were established using aqueous standards in the conventional manner¹¹.

Initially, this involved digestion on a hot-plate but was unsatisfactory due to the length of time (several hours in some cases), potential problems of contamination, and incomplete digestion, particularly for the tobacco. The use of a microwave digestion procedure solved these problems and involved a modification of a previously established method for cadmium in fish¹². After digestion, the sample was diluted with deionized water to a known volume to ensure that it was on the linear part of a calibration curve. A typical procedure is shown in TABLE 1. Recoveries of selected metals (most commonly cadmium and lead but occasionally chromium) were in the 90-105 % range for several trials spiked into the digested cigarette parts.

RESULTS AND DISCUSSION

Typical results for the determination of cadmium and lead are shown in TABLE 2. The results of the cigarette smoke are the mean of five determinations, ranging from 11.05 - 15.66 ng/m^3 , relative standard deviation of 1.67 % for cadmium and 18.67-29.58 ng/m^3 , 4.23 % relative standard deviation for lead.

The concentrations in the inert cigarettes were obtained using three cigarettes with a typical standard deviation of < 2%. In general, there is about twice as much lead as there is cadmium in both the cigarette smoke and inert cigarettes. For both metals, the concentrations are still relatively low. A comparison to the 21-year study (1968-1988) of Canadian cigarettes⁴, showed a decrease in lead concentrations from 3.68 to 1.92, cadmium from 2.89 to 2.22 $\text{mg}/\text{cigarette}$; 216 to 83 for lead, and 271 to 164 $\text{ng}/\text{cigarette}$ for

TABLE 1. Digestion Procedure for Inert Cigarettes

Mass (g)	HCl (ml)	HNO ₃ (ml)	Digestion time (s)
Whole cigarette	2.18	10.0	10.0 3.0
Filter	0.32	10.0	10.0 3.0
Paper	0.21	5.0	10.0 3.0
Tobacco	1.65	10.0	10.0 3.0

TABLE 2 Results of Cadmium and Lead in Cigarette Smoke and Cigarettes

Whole cigarette	17.56 mg/g of Cd	31.94 mg/g of Pb
Filter	2.56 mg/g of Cd	8.74 mg/g of Pb
Paper	3.05 mg/g of Cd	4.26 mg/g of Pb
Tobacco	11.87 mg/g of Cd	18.44 mg/g of Pb
Cigarette smoke	13.41 ng/m ³ of Cd	25.72 ng/m ³ of Pb

cadmium in cigarette smoke. The values obtained for the individual parts of the cigarette in this study were about an order of magnitude higher than that obtained in the Canadian study.

CONCLUSION

It is probable that the concentrations of the metals in the cigarettes originate from the soil and in the manufacturing process. In general, cigarettes are a blend of several tobaccos from several different sources and it would be difficult to pinpoint the sources of cadmium and lead. It is interesting to note that the concentrations are still relatively low, mg/g in the inert cigarettes and ng/m³ in the cigarette smoke. However, it should be noted that the levels of ng/m³ were obtained from a few seconds of cigarette smoke. A cigarette will generate smoke for (typically) a few minutes, and the amount of smoke from one cigarette may be in the order of a few micrograms per cubic meter per cigarette. Impaction-GFAAS is too sensitive a technique for cadmium and lead at these concentrations. Balanced studies

between concentrations of metals in inert parts of a cigarette and in smoke from a whole cigarette could reveal an interesting correlation. This work is currently under consideration.

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