P A R C
AN AUTOMATED APPARATUS FOR CLEAN-UP PROCEDURES USED IN PCDD/F- AND CHLOROBENZENE-ROUTINE-ANALYSIS

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ABSTRACT

PARC (Processor for Automatic Routine Clean-up) is a concept to automate and control complex liquid chromatographs. It has been developed for the requirements of routine laboratories. Pivotal is a control software, which assists a particular control programming language, an user definable screen and a programmable dialogue with the operator of an application. The language has been constructed with the aim to get an easy programmable time controller and to create applications, which can be handled easily by the laboratory personnel.

The controller is utilised in our laboratory for clean-up procedures of polychlorinated dioxins and furans (PCDD/Fs) and chlorobenzenes from extracts of waste incinerator fly ash. Clean-up procedures according to VDI-guidelines were chosen. The automated alumina column clean-up proved to be highly reproducible with recoveries mainly higher than 90%.

INTRODUCTION

Many successful efforts have been made in automation of the quantitative analysis of environmental relevant toxins like PCDD/Fs and related compounds.

Several examples for the automation of different clean-up methods in PCDD/PCDF-analysis have been published[1-3]. The methods were focused on matrices as human serum and adipose tissue[1,2] and milk[3]. A control language for robots has also been published[4].

PARC CONTROL SOFTWARE

The PARC control software is an universal tool for time control of chromatographic units. The software qualifies a central personal computer (IBM-PC and

compatibles, MS-DOS operation system) to communicate with up to 62 chromatographic units (HPLC/MPLC-pumps and actuator driven valves). The hardware components, purchased from *Kronwald Separation Technik, Sinsheim, Germany*, are interconnected by a RS-232-interface cable in tandem and are driven by one single RS-232-interface, connected to the computer.

The PARC control software is an interpreter, written in the C programming language. It provides a set of commands, which can be subdivided into five groups; in detail, commands for controlling peripheral units, commands for the dialogue and time control, screen commands, program structure commands, and commands for communication via PC ports. In our application the PARC software controls prewashing, preelution of columns, it assists the sample injection procedure and performs all elution steps automatically. After sample injection, observation of the process is not necessary. The configuration of the assembly and the actions of the components are visualised on a graphic screen.

PARC LIQUID CHROMATOGRAPHY HARDWARE CONFIGURATION

The components of liquid chromatography are combined in a modular manner. The flow scheme in figure 1 outlines the configuration of the apparatus for clean-up of PCDD/Fs and chlorobenzenes. The apparatus processes up to five samples sequentially. Each sample will be assigned to a specific column. Block 1 provides the chromatographic pump and the motor driven valve for selecting the solvents. Block 2 contains two motor driven valves and five manual valves serve as a sample injection unit. The alumina columns as used in

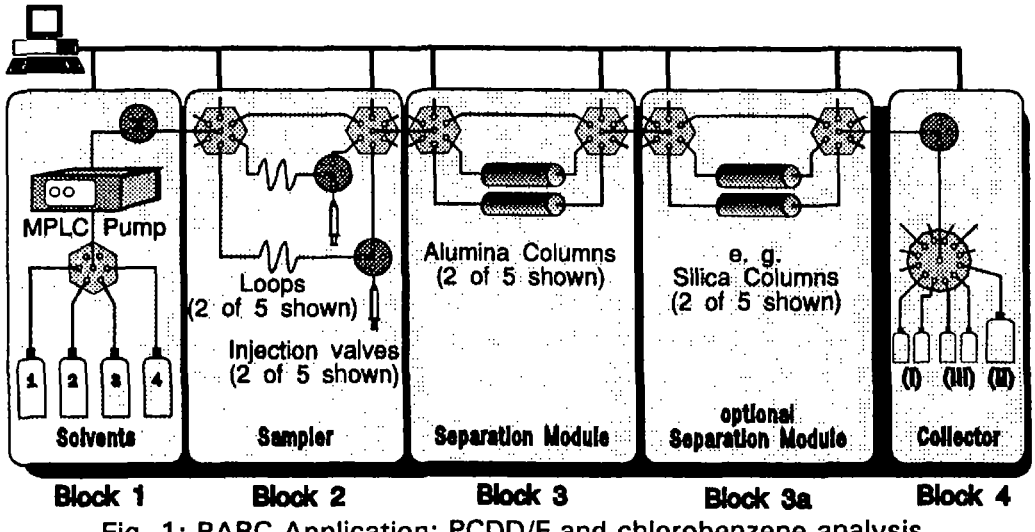

Fig. 1: PARC-Application: PCDD/F and chlorobenzene analysis

our experiment are located in block 3. When multiple clean-up steps are desired, different column blocks can be interconnected as indicated in the figure (block 3a). At least one motor driven valve serves as fraction collector in block 4. Eluates are collected in TurboVap 500 tubes (*Zymark, Idstein/Ts, Germany*) for automatic evaporation[5].

VALIDATION STUDIES

To perform a validation of the automated method, the recoveries of PCDD/PCDFs and chlorobenzenes in fly ash from a municipal waste incinerator were determined. The automated procedure is derived from VDI-guidelines[6] and earlier publications[7,8].

Preliminary an amount of 15 g ground fly ash was treated with hydrochloric acid and extracted with 100 ml of toluene. The solution was concentrated and divided into aliquots. The content of all 2,3,7,8-substituted PCDD/Fs and dichlorinated to hexachlorinated benzenes in the extract was quantificated five times by using internal ^{13}C-surrogates according to VDI Clean-up procedures[6].

Subsequently the determination of the recoveries of all degrees of chlorination of the PCDD/Fs and chlorobenzenes was performed as follows. An aliquot (750 µl, equalling 3 g fly ash) was automatically applied on one of the alumina columns (12 mmØ, 15 g alumina, *alumina B super I, ICN Biomedicals, Germany*). The chlorobenzenes were eluted with 50 ml benzene. After washing with 120 ml of hexane/dichloromethane 98:2 (v/v), the PCDD/Fs were eluted with 125 ml hexane/dichloromethane 1:1 (v/v). All elution steps were performed with a flow rate of 2 ml per minute. The contents of all 2,3,7,8-substituted PCDD/PCDFs and all dichlorinated to hexachlorinated benzenes were determined by adding ^{13}C-surrogates *after* the clean-up procedure, followed by standard GC/MS analysis[6]. The experiments were repeated five times to get mean values. The recoveries were obtained as quotient of the mean values and the original contents of the extract.

RESULTS AND CONCLUSION

The clean-up recoveries of the automated procedures (mean and standard deviation of 5 experiments) are shown in figure 2.

The mean recovery for all PCDD/Fs was found to be 89.7%. The standard deviation was on average 3.2%. A recovery of 90.6%±3.6% was obtained for the chlorobenzenes.

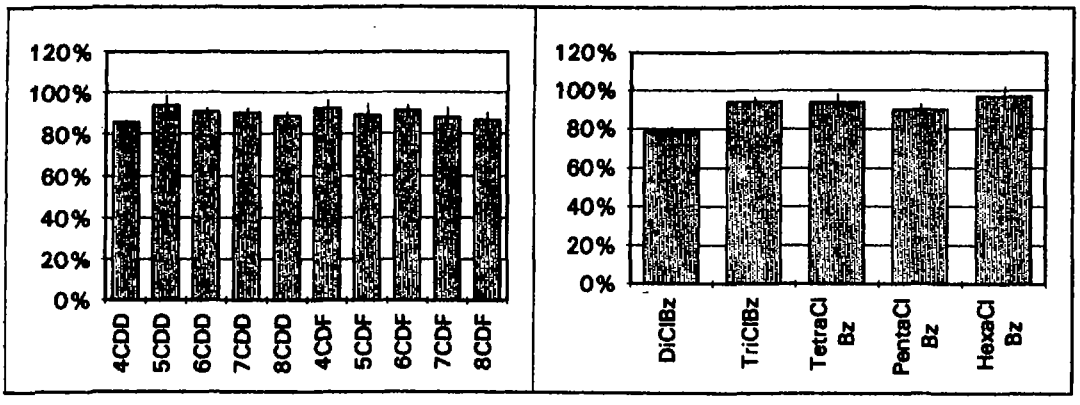

Fig. 2: PARC, alumina clean-up: recoveries of PCDD/Fs and chlorobenzenes.

For the application of the PARC unit we see the following advantages:

- no need of personal observation of the elution step,
- the process can be run overnight,
- high rates of recovery,
- high reproducibility.

We conclude that the automation of clean-up procedures is advantageous even in clean-up procedures for matrices as easy to handle as fly-ashes.

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