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Information support for the incineration of chemical waste in cement kilns

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Abstract

A specialised information system on industrial (hazardous) waste management has been developed and applied in Slovenia. It is composed of (1) computerised waste registry, (2) reference database on waste and waste water management, (3) relational database on river water pollution, (4) a prediction of waste generation module, and (5) an expert system for determination and prevention of river water pollution. Incineration of hazardous waste in cement kilns was identified as an efficient solution for over 20% of chemical waste accumulated. A specialised database on analytical control for this incineration was created, with the files on sampling, sample preparation, waste characteristics, and methods for proximate, survey and directed analyses. The method of structuring information into systems for the recognition of relationships and patterns was applied, resulting in a model system for analytical control of waste incineration in cement kilns presented in Fig. 4. The vertical branches of the system give the succession order of analyses for (1) cement raw materials, (2) primary fuel, (3) waste blended as secondary fuel, (4) stack gas, (5) dust from electrofilters, and (6) cement produced. The hierarchical organisation enables recognition of key analyses and pathways, as well as of optional procedures.

1. Introduction

The efficiency of research and development can be considerably increased by organising information, which is usually available in bits, into well-structured schemes. The structuring of information enables a better definition of parameters and recognition of their hierarchical order and relations. This can lead to the design of patterns of knowledge which enables hypotheses of higher probability to be formed [1, 2].

For the structuring of information into patterns of knowledge, comprehensive information must be available. If a problem is of a complex nature, the amount and diversity of information should be high, and a computerised information system is needed. This is certainly true for chemical (hazardous) waste management.

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2. Specialised information system on chemical (hazardous) waste management

In the effort to find high efficiency and low cost solutions to the chemical waste problem which had accumulated in Slovenia, a highly specialised information system was first developed [3, 4] (Fig. 1). The system is intended to support research, development and environmental decision making. It is installed on PC which enables wide transferability. The system is fed by collection and analysis of primary documentation from national and international sources. The results are compared and completed by processing six international databases.

2.1 Information system for special waste management

The Waste Registry is a factual relational database covering the specific needs of the Republic of Slovenia with two million inhabitants and a chemical industry with about ten thousand employees. This database includes statistical data on (1) waste generators, (2) waste processing and waste disposal options based on Republic waste regulations, (3) qualitative and quantitative characteristics of waste, (4) waste storage, processing and final disposal, and (5) production processes generating waste needed for building of waste generation prediction models.

The system was built using dBASE III PLUS and CLIPPER programming language on IBM compatible PC as relational databases consisting of five modules. The connection among modules is provided by a waste and company coding system. Recently the system has been transferred into PARADOX version 3.5 database management system, and modules links were provided by the PASCAL programming language.

The processing of the Registry enables the recognition of several dimensions of the waste problem, e.g. accumulation of different types of waste in different locations, trends in waste generation, relationships between total quantities of raw materials, products and total waste generated, etc. The information provided by the Registry serves in the planning of waste minimisation, waste transport, blending and incineration.

2.2 Reference database on waste and waste water management

These segments are built on IBM compatible PC using UNESCO CDS/ISIS Information Storage and Retrieval System, and connected via keywords. This software package also enables the non-specialist user to have easy access to all segments of the reference database.

2.3 Bibliographic database

This covers printed publications (selected books, scientific papers, patents, standards, industrial reports, project reports, regulations, etc.), as well as "grey" literature (e.g. theses). The database is regularly updated by target-oriented search and selection of new information. It contains over 4500

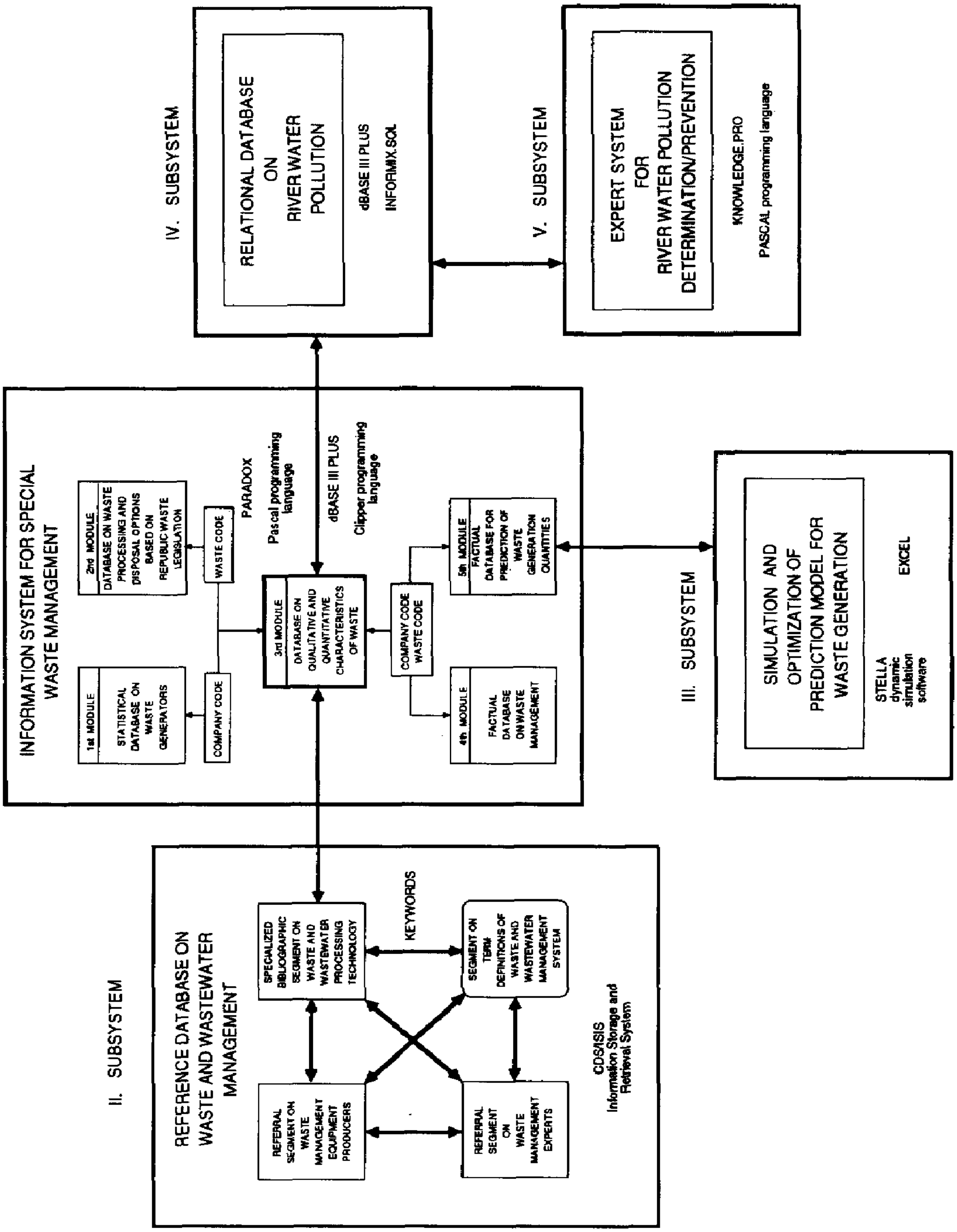

Fig. 1. Integrated information system for pollution determination and prevention.

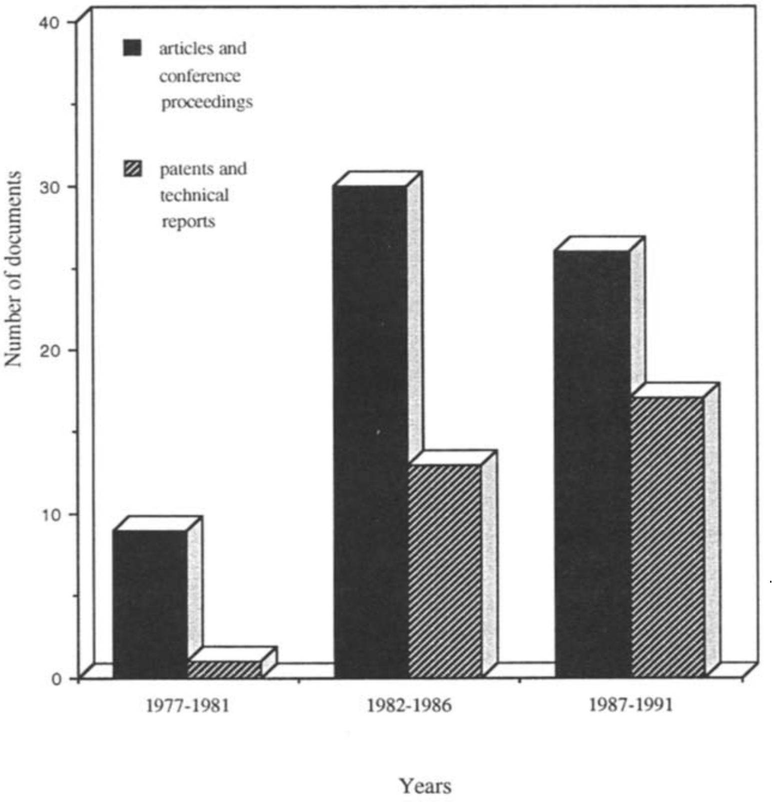

Fig. 2. Number of documents on hazardous waste incineration in cement kilns by types and years.

documents (January 1992) and has been accessible on-line from 1988 on the national host IZUM at the University of Maribor.

The processing of the database not only provides information for selected questions, but also enables trends to be followed. An example is given in Fig. 2.

3. Information database on the analytical control of waste incineration in cement kilns

In countries burdened by economic crises, which is particularly serious in Eastern/Central Europe, there is little hope of acquiring investments into special waste incinerators which cost 50 million U.S. dollars or more [5]. There is also a strong "green peace" movement against transborder transport of hazardous waste, for which some claim that it would bring foreign investors to the country. The incineration of waste in cement kilns seems to be more realistic. Cement industries are widely available in most countries, and the investment in adaptation of cement kilns is less than 2 million US$. Cement kilns are reported to enable high destruction of organic hazardous constituents (greater than 99.99%) [6], neutralisation of acid gases by alkaline clinker, long retention time, absorption of toxic metals into non-leaching mineral matrices of clinker, no residues and considerable energy savings [7]. Waste organic solvents, used motor oils, as well as cooling and lubricating oils, and even pulverised waste can all be incinerated. The wet cement production process is also suitable for concentrated residual waste waters that contain small amounts of combustible organic compounds. They can be added to the raw mix feed [8–11].

However, there is an *a priori* mistrust from the cement producers and consumers who are worried about the deterioration of production lines and product quality, and, in particular, of the general public who may fear air and water pollution linked with health hazards [12]. A thorough analysis of the initial situation, and setting up regular control of the incineration of chemical waste in cement kilns is therefore a *conditio sine qua non* [13, 14].

A detailed study of the available documentation on analytical methods and techniques for the control of chemical waste incineration in cement kilns was carried out first, and a database on analytical procedures built. Based on the study of EPA regulations pertaining to this field [15], a specialised database "Sampling, sample preparation and analysis" has been built. The database was designed for an IBM compatible PC, using software package CDS/ISIS.

The following *structure of records* was designed.

1. *Method number*
   Each method is marked with a 4–5 character code.
   The first character is a letter denoting the field of activity:
   - S–sampling methods
   - P–sample preparation procedures
   - C–analytical methods for determination of waste physical characteristics
   - A–analytical method for determination of waste chemical characteristics

   In these specific fields the methods are described with a three character number and sometimes also by a letter (a, b, c) denoting the method variant.
2. *Method name*
   From the method name, which is taken from the original document, it is usually possible to determine target compound(s) and the main analytical method used.
3. *Analytical method*
   One or more main analytical methods are listed (e.g. liquid/liquid extraction, GC/MS).
4. *Matrix*
   Matrices for which the method is applicable are listed.
5. *Analytical equipment*
   This field includes basic data on necessary analytical equipment and is divided into three subfields:
   - ^t–apparatus type, general name of apparatus (e.g. HPLC/UV, graphite furnace)

^**i**–exact data on the producer and model of apparatus if at all mentioned in primary document
^**o**–other data not applicable to other two subfields

6. *Parameters of analytical methods*
Text field with a more detailed description of each analytical method, including equipment parameters (e.g. for GC exact data on column, working temperature, carrier gas).
7. *Detection limits of analytical method*
The field consists of four subfields:
^**e** – unit of detection limits, e.g. mg/l, ppm
^**n** – lower detection limit
^**x** – upper detection limit
^**o** – other additional data
8. *Compounds and standards*
The field contains the list of compounds for which the method is applicable, or a list of suitable standards.
9. *References*
The field contains basic data on primary documents describing the method.

The database consists of 98 records on methods in both English (ANI) and Slovene (ANS) versions. The database files are:

1. File: Sampling (12 records)
2. File: Sample preparation (22 records)
3. File: Analysis of waste (64 records)
   3.1. Subfile: Waste characteristics (4 records)
   3.2. Subfile: Waste analysis (60 records)
      3.2.1.: Proximate analysis (6 records)
      3.2.2.: Survey analysis (8 records)
      3.2.3.: Directed analysis (46 records)

The structure of the database is shown in Fig. 3.

1. *File*: *Sampling*

In this file standard methods for sampling waste and stack gases are described. Methods of stack gas sampling are divided into: (1) continuous sampling (O_2, CO, CO_2, SO_2, NO_x, TOC); (2) EPA–MM5 method of sampling of solid particles, organic substances, metals and chlorine; (3) VOST method of sampling volatile organic substances, found in stack gas in low concentration.

2. *File*: *Sample preparation*

The collected sample, regardless of its state of matter, must be converted into a matrix which is compatible with the final analysis methods needed for measurement of the designated POHC(s). The types of samples which could be collected during the evaluation of a hazardous waste incineration include: (1) permanent gases and stack gases collected as comprehensive sampling train components, (2) liquid samples: aqueous liquids (including process waters) and organic liquids, (3) sludges (including suspensions, slurries, and

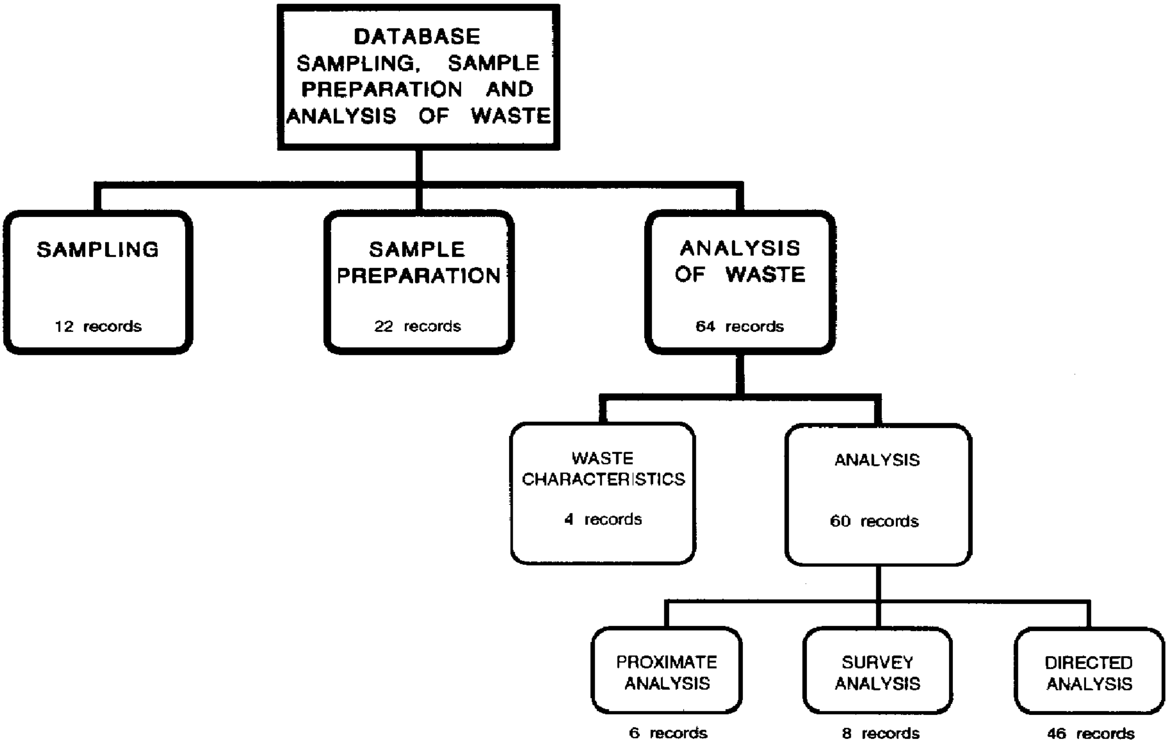

Fig. 3. Structure of the database "Sampling, sample preparation and analysis".

gels), (4) solids (including particles from filters, solid residues, and sorbents). Methods described in this file are divided into: (1) preparation of representative aliquots from field samples, (2) recovery measurements, (3) sample extraction of organic compounds, (4) concentrating solvent extracts, (5) digestion for metals' analysis, and (6) sample cleanup procedures.

3. *File*: *Analysis of waste*

This file refers to waste and by-products of incineration. In the first part, methods for determining basic waste characteristics are given for ignition, corrosivity, reactivity (explosivity, possible reactions with other substances) and toxicity based on leaching tests.

The second part describes analytical methods for determining waste composition and by-products of incineration. The composition is analysed in three steps: proximate analysis, survey analysis and directed analysis. Proximate analysis defines consistency (viscosity), calorific value, humidity content, dry matter and ash, and elemental composition (carbon, hydrogen, nitrogen, sulphur, phosphorus and halogens). Elemental composition is essential for the prediction of possible hazardous organic compounds in waste. This segment is supported by a referral database "Chemical Compounds Characteristics" [16]. The database contains data relevant for incineration of 362 organic compounds which are frequently present in waste. With the combination of element composition and the data on compounds in the database, it is possible to predict possible hazardous organic compounds in waste.

Following proximate analysis, the content of organic and inorganic substances, especially metals in waste, are determined by survey analysis. During experimental incineration of waste the content of organic and inorganic substances is determined with by-products of thermal destruction in stack gas [17].

Since it is not possible to control quantities of all organic compounds in waste, one to a maximum of six hazardous substances in waste are selected [12], based on the results of proximate analysis, POHC (Principal Organic Hazardous Constituents). The destruction factor and removal efficiency, DRE, is determined [18, 19].

By directed analysis by-products of incineration of selected POHC compounds in stack gas samples are determined, after which the DRE factor can be calculated.

4. Structuring of information into systems: An example for analytical control of waste incineration in cement kilns

The aims of structuring information on analytical procedures for the control of waste incineration in cement kilns were:
(1) *to identify the existing methods* for sampling, sample preparation and analyses in order to determine parameters which influence environment or product quality, either in input (raw materials, primary fuel and secondary fuel from waste) or output (cement, stack gas, electrofilter and other ash, scrubber solutions);
(2) *to develop a hierarchical structure* of these procedures which would show gaps and call for amendments with additional or alternative procedures; and
(3) *to recognize key analyses* for monitoring an environmentally and production-wise safe process, the frequency of their application, and the cost of analyses.

4.1 Identification of methods

The basis for the first draft structuring were sampling and analysis methods for hazardous waste combustion, identified by EPA [15]. Apart from methods for determination of dangerous/toxic compounds in special/hazardous waste and stack gas, the scheme also incorporates appropriate methods for determining parameters, which can have impact on environment and/or product quality for raw materials, primary fuel (coal), electrofilter or other ash, scrubber solutions and product (cement) [12].

The above methods [15] are mostly standard ASTM (American Society for Testing and Materials) and official EPA methods. Other standard methods for sampling, sample preparation and analytical methods, collected from different sources, e.g. other ASTM, VDI (Verein Deutscher Ingenieure, Germany) [20], UNICHIM (Associazione per l'Unificazione nel Settore dell'Industria Chimica, Italy) standard methods, were incorporated in the scheme. They filled the gaps in the scheme or represent alternatives to existing methods.

4.2 Development of a hierarchical structure

After identification of relevant methods, the basic structure of the scheme was set up. Appropriate horizontal and vertical lines were identified. The *horizontal lines* in the scheme are:

- sampling
- sample preparation
  - representative aliquots from field samples
  - surrogate addition to aliquots for organic analysis
  - preparation procedure for determination of metals
  - extraction of organics
  - determination of total chromatographable organics
  - concentration of extracts
  - extract purification
- analysis
  - determination of basic waste characteristics
  - proximate analysis
  - survey analysis
  - directed analysis

The *vertical lines* include input and output from the cement production process, using special/hazardous waste as a secondary fuel:

- raw materials
- primary fuel (coal)
- secondary fuel (special/hazardous waste)
  - solids
  - sludges
  - organic liquids
  - aqueous liquids
- incineration by-products
  - stack gas
    - gas
    - scrubber solutions
  - electrofilter or other ash
- product (cement)

By verticals it is possible to follow appropriate methods for determination of relevant parameters from sampling to directed analysis (Fig. 4, Tables 1 and 2).

4.3 Recognising key analyses — Identifying levels of analysis

Methods in the scheme are arranged in three levels according to their sequence, relevance and accuracy:

(1) Obligatory procedures: It is necessary to carry these out for every charge of waste at its incineration. They include key methods ("fingerprint" analyses) for determination of parameters important for dosage of secondary fuel (waste)

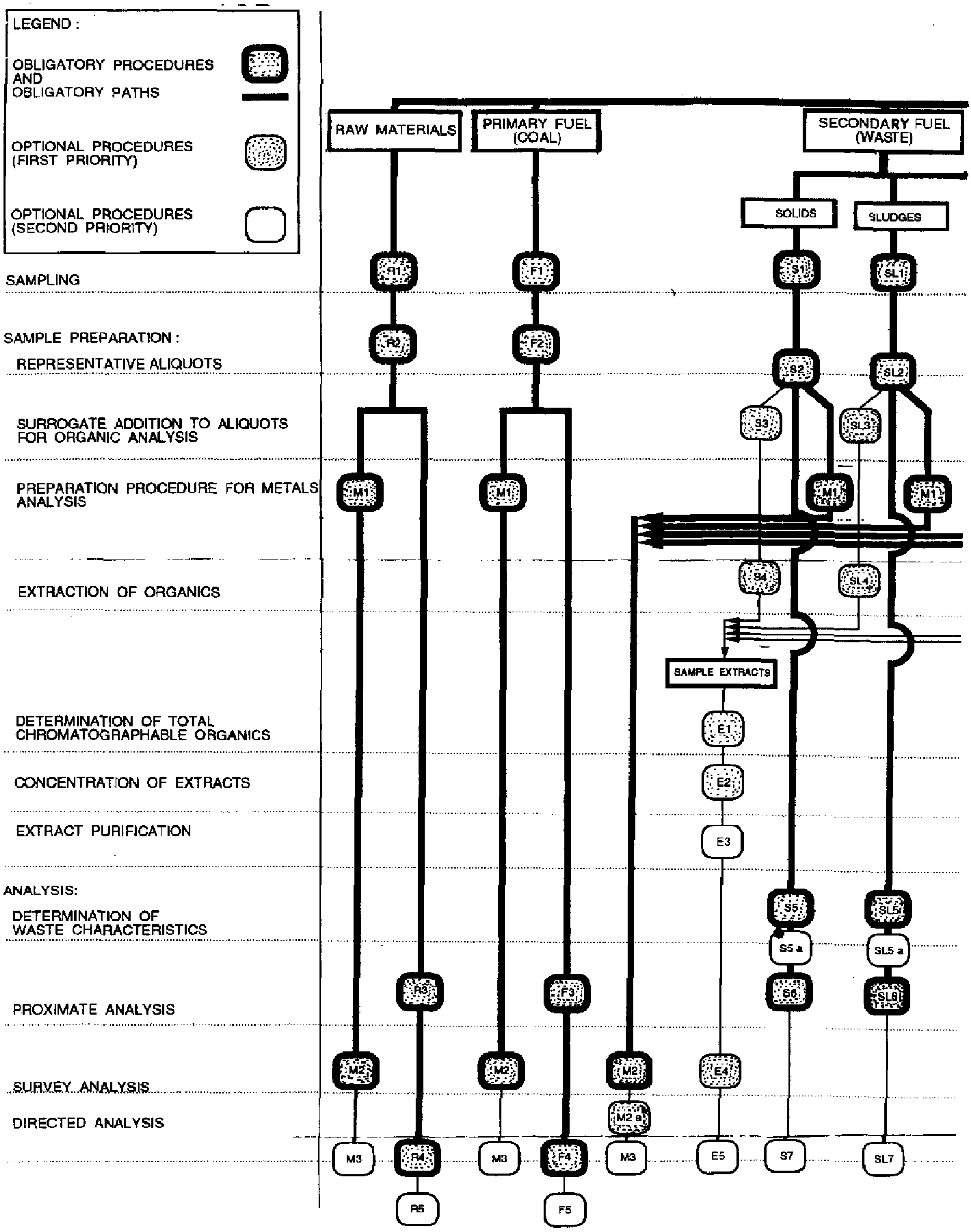

Fig. 4. Analytical procedures at waste incineration. (See Table 1 for legend.)

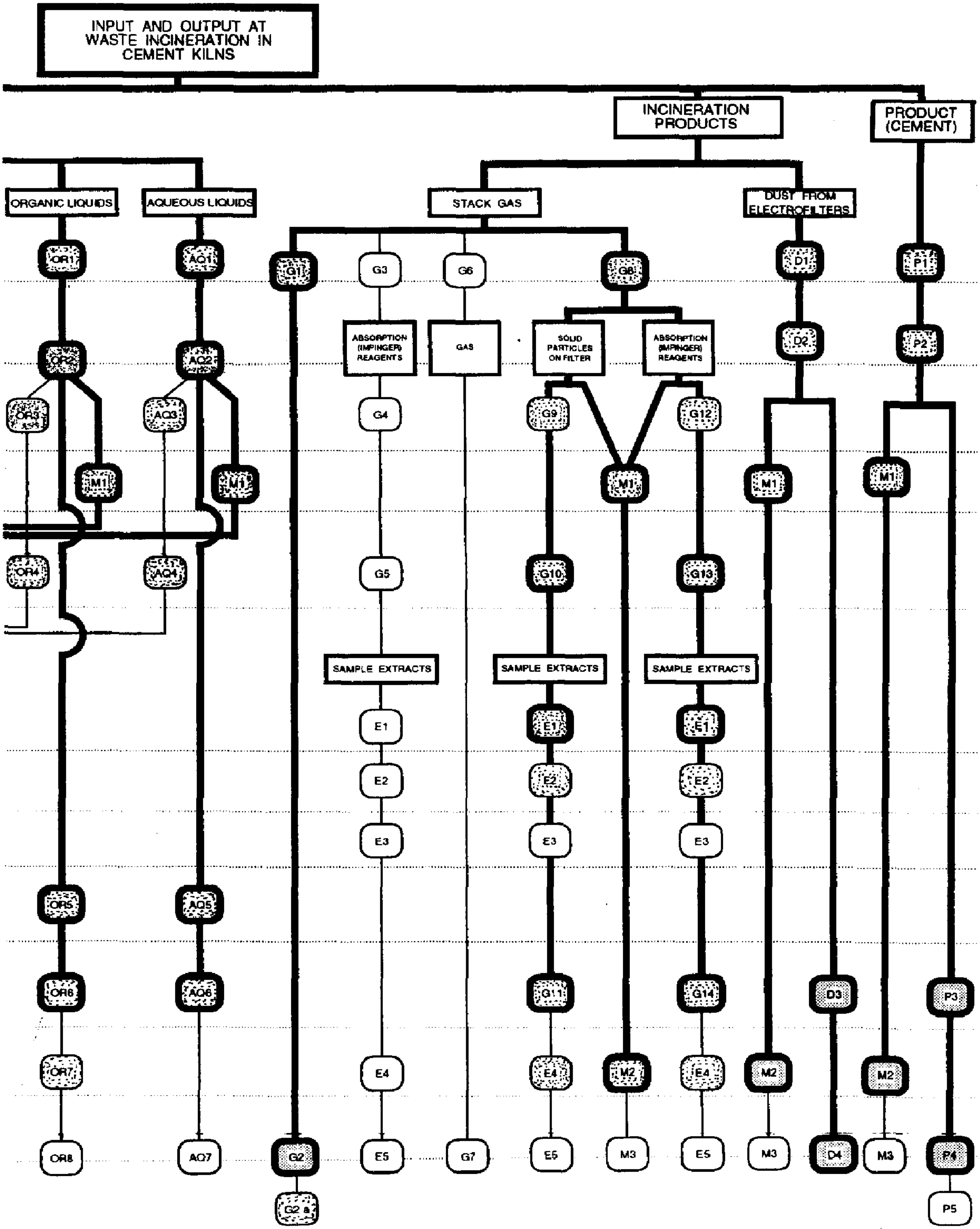

Fig. 4. Continued.

TABLE 1

Analytical procedures at waste incineration

Raw materials				
R1	R2	R3	R4	R5
5,6	15	39–41	102–105	106

Vertical in the scheme (Figure 4)
Code in the scheme (Figure 4)
Number of applicable methods (Table 2)

Primary fuel (coal)				
F1	F2	F3	F4	F5
5, 6	15	41 100, 101	102–105	106

Solids							
S1	S2	S3	S4	S5	S5a	S6	S7
5–7	15	16–19	25–27	35–37	38	39–41 44	56, 81–95, 97, 98

Sludges							
SL1	SL2	SL3	SL4	SL5	SL5a	SL6	SL7
6	14	16–19	22, 23	35–37	38	39–41 44	56, 81–95 96, 97

Organic liquids							
OR1	OR2	OR3	OR4	OR5	OR6	OR7	OR8
1–4	13	16–19	24	35–37	39–41 43, 44	47, 48	53, 63, 70–73 75–79 81–95, 97

Aqueous liquids						
AQ1	AQ2	AQ3	AQ4	AQ5	AQ6	AQ7
1–4	13	16–19	20, 21	35–37	39–44	54, 60–63 81–95, 96

TABLE 1. Continued

Stack gas							
G1	G2	G2a	G3	G4	G5	G6	G7
109	110–113	108, 114	12	16–19	20, 21, 24	10, 11	64–69 74, 80
G8	G9	G10	G11	G12	G13	G14	
8, 9, 99	16–19	25–27	41, 42	16–19	20, 21, 24	41, 42	

Dust from electrofilters			
D1	D2	D3	D4
5, 6	15	39–41	102–104 106, 107

Product (cement)				
P1	P2	P3	P4	P5
5	15	39–41	102–105 107, 108	106

Analysis of metals			
M1	M2	M2a	M3
29	52	81–95	104, 106

Analysis of extracts				
E1	E2	E3	E4	E5
45	28	30–34	46–52	57–61 70–73 75–79, 96

and/or blending different kinds of waste according to its moisture, solid and ash content, heating value, elemental composition, metals content. These results together with data on the waste origin are usually sufficient for determination of incineration parameters.

(2) Optional procedures (first priority): Their implementation depends on (a) properties of the sample (as determined by obligatory procedures), (b) special requirements for following some of the parameters and (c) in the case when the results of the obligatory procedures fall out of the usual value range (at "fingerprinting"). Among these procedures are also methods for survey analysis of organics (e.g. GC/MS, IR). It is recommended to carry out one of them for every charge of waste to be incinerated.

(3) Optional procedures (second priority): These procedures are carried out (a) at thorough analysis of new sample (primary characterisation to determine "fingerprint" parameters and their value ranges), (b) to follow some of the

TABLE 2

Methods for sampling, sample preparation and analysis

No.	Method name
1	Coliwasa
2	Dipper (pond sampler)
3	Weighted bottle
4	Tap
5	Thief (grain sampler)
6	Trier (sample corer/waste pile sampler)
7	Trowel (scoop)
8	MM5 train
9	SASS train
10	Gas bulb
11	Gas bag
12	VOST–Volatile Organics Sampling Train
13	Representative aliquots from field samples
14	Representative aliquots from field samples
15	Representative aliquots from field samples
16	Surrogate addition to aliquots for organic analysis
17	Surrogate addition to aliquots for organic analysis
18	Surrogate addition to aliquots for organic analysis
19	Surrogate addition to aliquots for organic analysis
20	Extraction of semivolatiles from aqueous liquids
21	Extraction of volatiles from aqueous liquids
22	Extraction of semivolatiles from sludges
23	Extraction of volatiles from sludges
24	Semivolatiles from organic liquids
25	Extraction of semivolatiles from solids
26	Extraction of semivolatiles from solids
27	Extraction of volatiles from solids
28	Drying and concentrating solvent extracts
29	Digestion procedure for metals
30	Florisil column chromatography
31	Biobeads SX-3
32	Silica gel chromatography
33	Alumina column chromatography
34	Liquid/liquid extraction
35	Ignitability
36	Corrosivity
37	Reactivity
38	Extraction procedure toxicity
39	Moisture, solid and ash content–macroscale
40	Moisture, solid and ash content–microscale
41	Elemental composition–organic
42	Total org. carbon (TOC), total org. halogen (TOX)
43	Viscosity
44	Heating value of waste
45	Organic content by TCO
46	Organic content by GRAV
47	Organic content–volatiles

TABLE 2. Continued

No.	Method name
48	Compound class type by infrared analysis
49	Mass spectrometric analysis
50	Specific major components by GC/MS
51	Specific major components–HPLC/IR or LRMS
52	Survey analysis for inorganics
53	Volatiles
54	Volatiles
55	Volatiles
56	Volatiles
57	Extractables
58	HPLC/UV–generalised procedure
59	HPLC/UV–generalised procedure
60	Aldehydes–derivatisation procedures
61	Aldehydes–HPLC analysis
62	Carboxylic acids
63	Alcohols
64	Phosphine
65	Fluorine
66	Gases–cyanogens and phosgene
67	Gases–mustard
68	Gases
69	Acid chlorides
70	Aflatoxins
71	Brucine
72	Citrus red No. 2
73	Cycasin
74	Ethylene oxide
75	2-fluoroacetamide
76	Lasiocarpine
77	Phenacetine
78	Strychnine
79	Oximes
80	Tris(1-aziridinyl)phosphine sulphide
81	Antimony
82	Arsenic
83	Barium
84	Beryllium
85	Cadmium
86	Chromium
87	Lead
88	Mercury
89	Nickel
90	Osmium
91	Selenium
92	Silver
93	Strontium
94	Thallium
95	Vanadium

TABLE 2. Continued

No.	Method name
96	Anions
97	Total cyanides
98	Phosphides
99	UNICHIM gas sampling train, Italy
100	ASTM D-240: determination of heating value
101	ASTM D-482: determination of ash content
102	ASTM D-808: chlorine determination
103	ASTM C-25: sulphure determination
104	X-ray determination of Na
105	X-ray determination of Mg
106	X-ray determination of K
107	Determination of dioxins and PCBs by GC/MS
108	Determination of organic compounds by TOC
109	Continuous sampling of gas
110	Continuous analysis of O_2
111	Continuous analysis of CO
112	Continuous analysis of NO_x
113	Continuous analysis of SO_x
114	Continuous analysis of CO_2

parameters (e.g. for DRE determination) or (c) for additional analysis, depending on the sample. Some of them can be also obligatory, according to regulations or special properties of the sample (e.g. determination of volatile organics in stack gases in USA by Volatile Organics Sampling Train) [21].

5. Conclusions

An integrated information support for hazardous chemical waste management can significantly contribute to waste reduction, the safety of waste storage and processing, and to the economic efficiency of these processes. The Computerised Waste Registry proved to be the first step, allowing for waste to be followed "from cradle to grave" and thus minimising the danger of inadequate waste disposal. Knowledge of locations and quantities of waste enables better planning of waste processing, and the information on the costs of the latter helps to highlight the need for waste reduction at the source. Bibliographic and reference databases catalyse the international transfer of waste management know-how and technologies.

Higher levels of information processing – particularly the structuring of information into systems for the recognition of parameter hierarchy, relations and patterns of knowledge – promote efficient application in the control of processes, as presented in this work and as illustrated by the example of cost-efficient analytical control design for the incineration of chemical hazardous waste in cement kilns.

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