Chemical Analyses of the Organic Portions of Household Refuse; the Effect of Certain Elements on Incineration and Resource Recovery

HARVEY ALTER

GEORGE INGLE

ELMER R. KAISER

Household refuse, often considered merely waste for disposal, is being considered as fuel for utility boilers [1], for chemical feedstock for pyrolysis to produce fuel gas and oil [2,3], and as media for anaerobic digestion by bacteria to produce methane [4]. Previous chemical analyses of this portion of municipal solid waste were directed only at incineration [5].

The organic portion of household refuse typically contains food residues, lawn and garden trimmings, wood, and a variety of paper and plastic products. The relative content of these materials may vary with climate and temporally with the season and even day to day, within a given week, subject to local habits [6]. An "average" municipal refuse may contain carbon 35.3, hydrogen 4.4, oxygen 28.2, nitrogen 0.42, sulphur 0.20, and non-combustibles 31.4 percent by dry weight [5]. The work reported here was directed at establishing the contents of selected elements in the organic portion of household refuse. The aim was to identify possibly those fractions which may contain a sufficient amount of one or more of these elements capable of forming acidic or other undesirable products upon subsequent chemical or biological processing. The elements of interest are carbon, nitrogen, sulphur, phosphorous and chlorine. These may be acid precursors during combustion of the refuse as a fuel in a power plant or incinerator and possibly during pyrolysis. The effect of each of these elements in bacterial processes, such as anaerobic digestion, is less clear, although there is no doubt that the form of nitrogen and sulphur supplied is important [7].

COLLECTION AND ANALYSIS

Household refuse was collected two days in August, 1972, at the curb of 60 private homes in New Castle County, Delaware. The neighbourhoods were chosen from census maps to represent different socio-economic groups. The methods of choosing the neighbourhoods, statistical weighting and pooling of samples, and so forth, were part of a separate study of refuse composition and not germane to the work described here. The refuse was hand sorted into 10 categories of organic materials and 10 of inorganic. The former, and the weight percentage in each category, are listed in Table 1. It must be pointed out there are judgmental aspects to refuse sorting. For example, there are usually food wastes adhering to metal cans, paper labels on glass bottles, and other mixed items. Methods of coping with such materials have been discussed [8]. In all, 1,675 kg of refuse were collected and sorted. Individual categories of the components were placed in polyethylene bags and stored at -7°C until processed for analysis.

All material in a given category was dried, ground in a hammer or knife mill, sieved, and reground to pass a 2 mm opening screen. Aliquots of the ground samples were taken by coning and quartering, and

Reprinted from Solid Wastes Management, the monthly journal of the Institute of Solid Wastes, Vol. 64, No. 12, December 1974.

submitted to two commercial laboratories for determination of carbon, nitrogen, sulphur, phosphorous, and chlorine contents. ASTM methods for coal and coke were used. Further details of the preparation for analysis have been given [9].

RESULTS

The amount of carbon, nitrogen, sulphur, phosphorous and chlorine in each refuse category is listed in Table 2 for samples taken each of the two collection days. In most cases, there do not appear to be real differences between days. Other cases probably illustrate the heterogeneous nature of municipal solid waste. The values listed are the average of duplicate determinations on composite samples from the 60 homes, except for chlorine, where the average of from two to twelve determinations is listed, each representing samples obtained by pooling waste from groups of homes in different neighbourhoods. The values listed in Table 2 for carbon, nitrogen, and sulphur generally agree with a similar, but less detailed, study for another city [10], and with the cumulative results from elsewhere [5].

The results for the chlorine contents of certain categories may be too high due to contamination by food wastes. A composite sample of plastic items from the waste was prepared and extracted with hot water until the extract no longer gave a white precipitate with 0.1 N silver nitrate. Titration of the extract, and calculation as chloride, indicated 0.55 percent of the original plastic weight was water-soluble chloride, representing 15.2 percent of the total chlorine in the composite plastic sample. No attempt was made to identify other elements which may be similarly extracted from the plastics or other fraction with water or other solvents.

Table 3 lists the weight percentage (dry basis) of carbon, nitrogen, sulphur, phosphorous, and chlorine of the organic portion of the refuse. The several paper and plastic categories have been pooled. The percentages listed as weighted averages according to the mass of refuse in each category. These results can be used to derive an ultimate analysis for the organic portion of the refuse: carbon 48.7, nitrogen 0.82, sulphur 0.26, chlorine 0.66, phosphorous 0.10 weight percent, dry basis. This calculated chemical composition, except for phosphorous, agrees with analyses of mixed refuse from four other locations [11]; no values for the phosphorous content for the latter locations are available. An analysis of refuse from a fifth location is reported as zero phosphorous [12]. The chlorine analyses in Table 3 have been reduced by 15.2 percent as a correction for water-soluble chlorides. This amount of chlorine is accounted for by adding to the amount reported for food wastes.

DISCUSSION

The role of chlorine and sulphur in the mechanism of corrosion of municipal incinerators was recently discussed; provided oxidizing conditions and certain temperature ranges are maintained in the heat exchangers and in the furnace proper, corrosion should be prevented [13]. These same conditions no doubt prevent major corrosion from the combustion products of carbon and nitrogen. Phosphorous as volatile phosphate has been measured in the flue gases of incinerators in concentrations of a few parts per million [9] and, not surprisingly, in much larger concentrations in the residue or slag [14]. Presumably, operating conditions could be established for utility power boilers to minimize corrosion from burning a mixture of coal and municipal refuse, recognizing the similarities and differences between coal and refuse as fuels.

In a recent report, Robertson [15] concluded that about 76 percent of the HCl emission from an incinerator comes from sources other than poly (vinyl chloride) and that sodium chloride in the refuse produces "very significant" quantities of HCl gas when incinerated. The data presented here support these findings.

Coals vary widely in composition. A "typical" bituminous coal (about 29×10^6 joules/kg, 10 percent ash) might contain sulphur 3 to 5, chlorine 0.05, and phosphorous 0.015 (calculated from the ash) percent by dry weight [16]. Except for the sulphur content, these values are lower than the corresponding values for waste fractions reported here. However, the current practice of mixing coal and waste to fuel a utility boiler [1], where the waste may not exceed 10 to 20 percent of the total fuel weight, is apt to maintain levels of the inorganic acid precursors in the fuel within ranges normally encountered in common coals.

After pyrolysis of wastes to fuel gases or oils, some or most of the nitrogen, sulphur, chlorine, or phosphorous in the waste is likely to be in the products. Compounds of these elements may affect the storage and handling of such fuels. However, it is likely that fuel produced this way will be available only in limited quantities and, as such, will be used to supplement fossil fuels. Thus, any effect on these

TABLE 1. COMPOSITION OF THE ORGANIC PORTION OF HOUSEHOLD REFUSE

New Castle County, Delaware, August, 1972

Category	Weight Percent[a]
Textiles	8.92
Wood	2.48
Garden	9.00
Rubber and leather	1.89
Food	16.45
Paper, general	21.40
Paper, packaging	12.08
Paper with metal foil[b]	0.22
Plastics, general	1.31
Plastics, packaging	2.03

[a] Dry weight basis. Remainder is a mixture of metals, glass, rocks, and other inorganic materials.

[b] Paper fraction only.

TABLE 2. CONTENT OF REFUSE CATEGORIES, DRY WEIGHT BASIS

	Weight Percent									
	Carbon		Nitrogen		Sulfur		Phosporous		Chlorine	
	Mon.	Thur.	Mon.	Thur.	Mon.	Thur.	Mon.	Thur.	Mon.	Thur.
Textiles	47.88	50.06	2.43	7.03	0.46	1.29	0.32	0.07	0.51	0.51
Wood	49.41	47.46	0.12	0.15	0.08	0.10	0.03	0.02	0.13	0.08
Garden Waste	47.87	40.11	1.36	1.95	0.08	0.27	0.16	0.20	0.19	0.36
Rubber and Leather	65.78	72.42	0.88	0.71	1.20	0.86	0.03	0.02	2.72	1.61
Food Waste	42.18	48.47	1.95	3.15	0.18	0.26	0.45	0.55	0.75	0.76
Paper, General	46.84	45.81	<0.01	<0.01	0.12	0.12	0.02	0.03	0.23	0.28
Paper, Packaging	45.08	44.27	<0.01	0.12	0.35	0.23	0.04	0.03	0.37	0.17
Paper with Metal (Paper part only)	42.92	44.26	<0.01	<0.01	0.06	0.05	0.04	0.08	0.17	0.20
Plastics, general	73.85	61.88	0.29	0.28	<0.06	<0.06	0.01	0.02	6.38	5.80
Plastics, packaging	80.42	79.00	0.31	0.37	<0.06	<0.06	0.01	0.02	2.24	2.90

TABLE 3. RELATIVE CONTENTS OF SELECTED ELEMENTS AS PERCENTAGE OF THE TOTAL

Dry Weight Basis
Organic Portion Only

Refuse Category	C	N	S	P	Cl
Textiles	7.29	43.35	25.64	13.38	5.55
Wood	4.74	0.80	1.75	1.07	0.73
Garden Waste	8.65	18.18	5.53	16.63	3.66
Rubber and Leather	5.81	4.10	17.14	1.05	14.17
Food Waste	9.21	29.31	8.23	49.62	17.04
Paper	54.39	1.80	40.19	17.28	22.98
Plastics	9.91	2.46	1.52	0.97	35.87
	100.00	100.00	100.00	100.00	100.00

elements on the combustion processes, or otherwise on the operation or corrosion of burners and boilers, will be diluted by the fossil fuel used.

Chlorinated hydrocarbons inhibit the formation of methane from hydrogen–carbon dioxide gas mixtures [17] and from sewage sludge [18]; a similar effect might be expected for methanogenic bacteria feeding on other wastes, if such chlorinated hydrocarbons are to be found in municipal solid wastes. Importantly, the effect of small amounts of inorganic chloride on these bacteria is unknown. The role of phosphorous is less clear; methane formation requires adenosine triphosphate (ATP), but the nature of this reaction or the mechanism of ATP synthesis in the methanogenic bacteria is presently unknown [16]. A study of volatile acids from anaerobic digestion did not include identification of any nitrogen containing acids, even when using a protein hydrolsate as the feedstock [17, 18]. It is likely that all of the elements discussed here, with the possible exception of chlorine, are essential to the life processes of the methanogenic bacteria. It should be determined if any of them are limiting to the formation of methane, especially the sulphur and phosphorous.

CONCLUSIONS

Previous reports of the contents of selected elements in refuse [5, 10] and the data reported here indicate that with little exception no one category of organic material from household refuse is a principal source of any one of the elements. Paper provides more than half of the carbon and also major fractions of the nitrogen, sulphur, phosphorous, and chlorine. These latter elements may be from food wastes contaminating the paper. Textiles are the largest single source of nitrogen (presumably from wool, acrylonitrile based synthetic fibres, and aminoplast resins used for textile finishing). Plastics supply slightly more than a third of the total chlorine. The small amount of sulphur in the waste came principally from the textiles, rubber, and paper.

At the present state of knowledge it is unlikely that the contents of nitrogen, chlorine, sulphur, or phosphorous in the organic portion of municipal solid waste will interfere with utilization of the waste as a source of fuel by direct burning or conversion to oils or gas by pyrolysis or to methane by anaerobic digestion. Also, small reductions in the content of any of the categories of organic materials is unlikely to have a significant effect on the total content of any of the elements investigated here.

ACKNOWLEDGMENTS

We thank John R. Lawrence for his assistance. This work was supported by the Society of the Plastics Industries, Inc. and the National Center for Resource Recovery, Inc.

REFERENCES

[1] D. Klumb, Solid Waste Seminar, *Proceedings* (Union Electric Company, St. Louis, 1972).

[2] G. M. Mallan and C. S. Finney, paper presented at 73rd Meeting, Amer. Inst. of Chem. Engineers, August, 1972.

[3] J. E. Anderson, U.S. 3,729,298, assigned to Union Carbide Corporation, April 24, 1973.

[4] J. T. Pfeffer, "Reclamation of Energy from Organic Refuse," final report to Environmental Protection Agency, grant R-800776 (Department of Civil Engineering, University of Illinois, 1973, 132 pp.).

[5] F. Bowerman in "Principles and Practices of Incineration", R. C. Corey, ed. (Wiley-Interscience, New York, 1969), p. 7.

[6] National Center for Resource Recovery, Inc., *Bulletin* 3 (No. 2) (1973), pp. 4-13.

[7] M. P. Bryant, S. F. Tzeng, I. M. Robinson, A. E. Joyner, Jr., in *Anaerobic Biological Treatment Processes,* Advances in Chemistry Series 105, R. Gould, ed. (American Chemical Society, Washington, D.C., 1971), pp. 23-40.

[8] E. R. Kaiser, C. Zimmer, D. Kasner, in *Proceedings of the National Incinerator Conference* (American Society of Mechanical Engineers, New York, 1970), pp. 25-31.

[9] E. R. Kaiser, "Acid Formers in Household Solid Waste," a report to the Society of the Plastics Industry, Inc., and the National Center for Resource Recovery, Inc., April, 1973, 38 pp.

[10] Institute for Solid Wastes, Amer. Public Works Association, Municipal Refuse Disposal (Public Administration Service, Chicago, 1970), p. 46.

[11] E. R. Kaiser, unpublished analyses for the feed to four incinerators: Valley Stream, N. Y., Lower Marion, PA, and Betts Avenue and Greenpoint incinerators in New York City.

[12] J. T. Pfeffer, *op. cit.*, p. 37.

[13] B. Baum, C. H. Parker, *Solid Waste Disposal,* Vol. 1, Incineration and Landfill (Ann Arbor Science, Ann Arbor, MI, 1973), chapter 13.

[14] G. H. Criss, A. R. Olsen, in *Proceedings National Incinerator Conference* (American Society Mechanical Engineers, New York, 1968), pp. 53-68.

[15] C. A. M. Robertson, *Solid Waste Management, 64,* 139 (1974).

[16] J. W. Leonard, D. R. Mitchell, eds., *Coal Preparation* (Amer. Institute of Mining Engineers, New York, 1968), chapter 1.

[17] B. C. McBride, R. S. Wolfe, in *Anaerobic Biological Treatment Processes,* Advances in Chemistry Series 105, R. Gould ed. (American Chemical Society, Washington, D.C., 1971), pp. 11-22.

[18] D.P. Chynowelt, R.H. Mah, ibid., pp. 4-54.