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Report on the Mission

DP/IND/88/015/11-65

(Nagpur, India: February 5, 1994)

of Dr. Ibolya Molnar-Perl, expert in the analyais of organic materials, present in Bayer cycles to India between 28 December, 1993 and 11 February, 1994.

for the

Jawaharlal Nehru Aluminium Research Development and Design Centre, Nagpur

Backstopping officer: Dr, T. Grof, Subsistance officer, UNIDO, Vienna.

Nagpur, February 5, 1994

Abstract

The mission was prepared by UNIDO Vienna in the frame of the Project "DP/IND/88/015/11-65" in order to assist the Government of India to realize a research and design activity of high level in the Jawaharlal Nehru Aluminium Research Development and Design Centre in Nagpur, India.

The aim of the mission can be summarized as follows:

- The presentation in theory and in praxis the main part of those achievements which have been obtained in the analysis of organics, present in alumina production in a more than ten years lasting research work, (for the time being not yet published, being a part of a Hungarian patent), performed at the L. Eotvos University, Budapest Hungary, supported by the Hungarian Research Institute FKI, Budapest, Hungary i.e.,:
    - to complete the necessary requirements to be able to start with the planned duties (apparata, glass wares, chemicals, etc.),
    - to hand over and to teach in those analytical methods that allow to control and to influence the damage of harmful organics, present in Bayer cycles, and,
    - to prove the utilization possibilities of the handed over methods by determining the organics, in terms of their quality and quantity, in the samples of the plants of 'Balco' and 'Nalco', respectively.
- In a frame of a Workshop, in the presence of Indian experts interested in alumina production, to call attention to the importance and to the possibilities how to handle organics of bauxites and their digestion products knowing their quality and quantity.

Nagpur, February 5, 1994.

Dr. Ibolya Molnar-Perl

Contents

Enclosures:

Activities

The activity of the consultant was based on the job desription and on the work plan and achievements obtained in JNARDDC

Time schedule of mission:

Arrival to Delhi from Budapest	December 28, 1993
Visit UNDP Delhi office	December 29, 30, 1993
Arrival to Nagpur from Delhi	December 31, 1993
Discussion of the scheme of our work plan with Dr. Janos Zambo and with Professor T.R.Ramachandran	
Work and teaching accordingly the plan (January 01 - February 09, 1994)	
Leaving Nagpur	February 9, 1994
Arrival to Budapest	February 10, 1994

Detailed work plan and achievements

The work has been performed in the presence and by the assistance of the following colleagues:

K. V. Ramana Rao, Ph. D.

Wasnik Kiran, M.S., and,

Mishra Raj Shekar, M.Tech.

January 1-8

The first eight days were needed

- to accomplish the accessories (apparata, glass wares, chemicals, etc.),

  and

- to prepare the laboratory, - provided for the organic analytical work, - to make it really suitable to the required purposes, i.e.,
  - -- to supply it with the necessary tap water and electrical power sources,
  - -- and to clean it to the unavoidable necessary extent.

January 9-20

The apparatus for the total organic carbon measurements has been brought from Hungary.

In spite of the fact that both the apparatus and the procedure can be regarded as simple ones, in order to handle the procedure it needs long experince, a continuous and many sided attention, as well as farreaching caution.

Miss. Wasnik Kiran seemed to be the colleague who was expected to be and proved to be the excellent person, (having M.S. degree from organic chemistry), to carry out these measurements.

The first laboratory tests were the total organic carbon balances of model Bayer cycles, performed in the bombes of JNARDDC with the highest success: it means that the synthetic aluminate liquor used for the model digestions proved to be kept in organic contaminant free conditions (Table 1).

As to the model Bayer cycles they have been performed with two bauxites stored in JNARDDC for a couple of months. As seen (Table 1)

- the 'Balco' balance proved to be acceptable within the experimental error of our technological and analytical measurements, while
- the two parallel 'Nalco' cycles also provided excellent accordance.

Meantime the presentation of the planned workshop lecture was also going on that took a considerable time and effort of the consultant.

January 21-31

Plant samples of 'Balco' and 'Nalco'arrived during this period of time

Beside the final installation of the gas chromatograph (GC) and that of the meantime received vacuum rotary evaporator also the organic carbon quantitation of the plant samples in terms of their total organic carbon- and humic acid contents were determined by Miss. Wasnik with the highest excellence.

February 1-9.

The qualitative and quantitative determination of the constituents of plant samples (Tables 2, 3), (performing their n-butyl esterification in the presence of the inorganic matrix), were teached in both to Dr. Ramana and to Mr. Mishra.

The handling of the GC and that of the data evaluation were excellently followed by Dr. Ramana.

Discussions on the ccrrespondig literature and theory of the processes were going on continuously.

Table 1

Organic balances of 'Balco'(46 g) and 'Nalco'(55 g) bauxites, taken in 1 Bayer cycle, digested of each by 120 ml synthetic aluminate liquor, at plant conditions.

BAUXITE CYCLE	BAUXITE	ALUM. LIQU	RED MUD	WASHING SODA	TOTAL	DISSOL -VED	%
`BALCO'1 IN	0.0415	0.0048			0.0463		
OUT		0.0293	0.00809	0.00547	0.0428	0.0348	75
`NALCO' 1a IN	0.0239	0.0048			0.0287		
OUT		0.0193		0.00397		0.0233	81
`NALCO' 1b IN	0.0239	0.0048			0.0287		
OUT		0.0194		0.0308		0.0224	78

TOTAL ORGANIC CARBON OF :

1.) BAUXITE g. / 100 g.

SOURCE	SINGLE	MEAN	R.S.D. %
BALCO	0.0921 0.0898 0.0945 0.0883	0.0902	4.3
NALCO	0.0409 0.0433 0.0463	0.0435	6.2

2.) SYNTHETIC ALUMINATE LIQUOR TAKEN FROM 4 BOMBS g. / l.

SINGLE	MEAN	R.S.D. %
0.044 0.042 0.036 0.045	0.042	9.6

Table 2.

Total organic carbon and humic acid contents of plant samples

	Plant	samples of	
The sample	BALCO		NALCO
	Expressed in	organic C g/l;	g/100g
	total	humic acid (%)*	total
bauxite	0.166	-	0.128
red mud	0.163	-	0.0750
red mud wash water	0.492	-	0.0750
prod. hydrate	0.016	-	
seed hydrate	0.105	-	
spent liquor	5.46	0.129 (2.4)	4.20
digestion liquor	7.50	0.204 (2.7)	
strong liquor	12.48	0.296 (2.4)	
pregnant liquor	5.40	0.243 (4.5)	
vanadium salt	1.164	0.0777 (6.7)	

* Expressed in the percentages of the total organic contents

Table 3.

Composition of the plant samples of 'Balco' identified and quantified as n-butyl esters

Acids:	Expressed in the %	of the total org. carb.
	strong liquor	vanadium salt
humic	2.4	6.7
formic	18.7	8.7
acetic	42.1	12.5
propionic	1.8	5.7
i-butyric	0.21	0.38
n-butyric	2.0	4.3
i-valeric	0.23	0.38
n-valeric	0.23	0.26
oxalic	7.4	32.5
benzoic	0.22	0.43
succinic	2.1	3.1
glutaric	1.2	1.1
adipic	0.85	<0.02
pimelic	0.27	<0.02
o-phthalic	1.0.	<0.02
hemimellitic	3.3	<0.02
trimellitic	0.30	<0.02
trimezic	0.35	<0.02
total	84.7	76.1

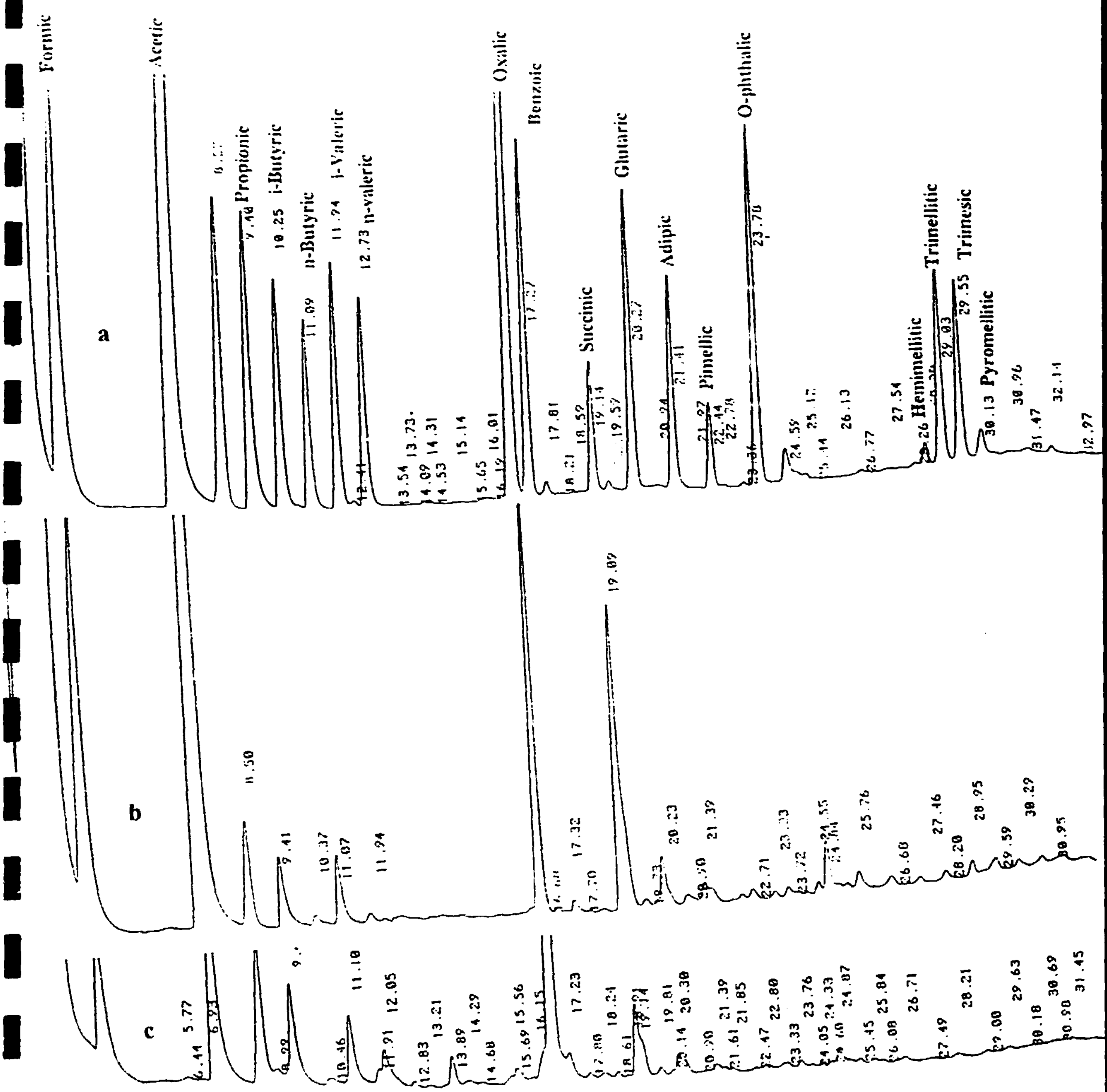

Figure 1 Gas chromatograms of the n-butyl esters of a model solution (a) and those of two 'Balco' plant samples (b strong liquor, c vanadium salt)

Recommendations

1. The laboratory provided for the analysis of organics should be used exclusively for this purpose:

The measurement of organic materials, present in the concentration range of 10^{-5} - 30 % needs in particular high cleanness:

- the laboratory shoud be kept free of organic contaminants,
- instead of the sweeping, accompanied by flying dust, the laboratory shoud be scrubbed every morning with clean tap water,
- similarly also the tables should be wiped with wetted cloth every morning.
- The total organic carbon quantitation shoud be performed only by Miss. Wasnik or exclusively by somebody else who was taught in by her.

2. The following items (accessories, glasswares) should be purchased or ordered imediately:

- gas cylinders of high purity nitrogen, pressed air and hydrogen,
- Australian syringes with changable needles (specification given),
- 1 ml pipettes of two marks,
- high temperature septa (specification given),
- quartz tubes for the total organic carbon apparatus (model is available).

ENCLOSURES

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

JOB DESCRIPTION*)

DP/IND/88/015/11-65

Post Title: Expert in Gas Chromatography

Duration: 1.5 months on site and 0.5 months homebase

Date required: 28 December 1993

Duty Station: Nagpur, India

Purpose of project: The immediate objective of the project is to assist the Government of India in setting up a functioning Aluminium Research, Development and Design Centre consisting of:

a) Alumina Production Research Department
b) Aluminium Electrolysis Department
c) Analytical Research Department
d) General Services, instrumentation and Control Department (incl. Workshop and Maintenance)
e) General Administration and Finance Department

The Centre will develop capability of carrying out the following main functions on behalf of and in co-operation with the bauxite processing/alumina production and aluminium smelter industries in the country:

a) Assimilation and adaptation of available technologies
b) Providing recommendations and ad hoc or applied and analytical research to local industries in process improvement, transfer of technology, etc.
c) Setting up and operating a data bank
d) Providing training of Indian engineers

Duties: The expert will be required to transfer theoritical knowledge , analytical methods and practice of qualitative and quantitative analysis of organics occuring in the Bayer-cycle, in frame of in-house training.

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*) *Applications and communications regarding this Job Description should be sent to:*
Project Personnel Recruitment Section, Industrial Operations Division
UNIDO, Vienna International Centre, P.O. Box 300, Vienna/Austria

Her main duties will be to:

1. Provide training for the counterpart staff of the centre in the determination of the total organic carbon content of the Bayer-liquors, bauxite and red mud.

2. Provide training on sample preparation for qualitative and quantitative determination of organic fractions by gas chromatography.

3. Provide training in qualitative and quantitative determination of different organic compounds present in Bayer-liquor by gas chromatography.

4. Analyse total organic carbon content of about 20 plant samples together with counterpart in order to determine the organic balances of two Indian (e.g. BALCO and NALCO) refinery. (Plant samples will be provided by the Centre).

The expert is expected to submit a Final Report after completion of the mission in 3 copies to UNIDO and 4 copies for the Government of India and the counterpart.

Qualifications:

University degree (preferably Ph.D.) in analytical chemistry with extensive practical and research experience in gas chromatography and its use in the aluminium industry.

Language requirements:

English

Background information:

The Indian aluminium industry looks back to a history of 44 years. The first aluminium smelter (in Alumpars, Kerala) was put into operation in 1943. At present there are five alumina plants in operation and six aluminium smelters with an overall capacity of about 587,000 and 580,000 tonnes per year, respectively. These facilities belong to five aluminium companies, namely Bharat Aluminium Company Ltd. (Balco), Hindustan Aluminium Corporation Ltd. (HINDALCO), the Indian Aluminium Company Ltd. (INDAL), the Madras Aluminium Company Ltd. (MALCO) and the National Aluminium Company Ltd. (NALCO).

With the commissioning of NALCO the share of the public sector in aluminium smelting is more than half of the total installed capacity of India. This indicates the decisive influence of the public sector on the future of the industry. The sustained growth and development of the aluminium industry in India, apart from requiring the adoption of suitable long term policies in relation to production management, output, pricing, and fiscal levies, is also in need for technology and market development, which will gradually be handled by the proposed Centre.

During the past years, India became one of the leading countries in the world having substantial bauxite resources, after the discovery of large deposits in the Eastern Coast in the nearly 1970s. The total bauxite reserves of India are estimated to be of the order of 2,650 million tonnes, which places India on the fifth place in the world list.

With the vast reserves of bauxite and coal in India, the aluminium industry has ambitious plans for a faster growth rate keeping in view the future demand in the foundry and export potentials.

The existing alumina/aluminium plants in India are based almost entirely on technology imported from various sources. Both in the areas of production of alumina and aluminium, a number of technological improvements have taken place in advanced aluminium producing countries. Import of improved technology is not always possible, also its introduction is not feasible in the existing plants. Import of technology necessitates proper assessments to determine its suitability under Indian conditions, the available raw materials, product demands, state of engineering developments, etc. Though research and development work is being carried out by the major aluminium producers in the country, these are mainly directed towards solving their day to day process problems in the plants. No work is done for the development of process know-how and basic engineering. The technologies followed in the existing plants are from various countries/suppliers - KAISER, ALUTERV-FKI, VAMI, ALCAN, MONTECATINI and ALUMINIUM PECHINEY. Apart from the strategic importance of having an indigenous Research, Development and Design Centre for Aluminium, the Centre is expected to save substantial hard currency payments to the foreign partners.

For meeting the estimated demand of aluminium by the turn of the century, substantial additional capacities for alumina and aluminium will have to be set up in the 1990s. Additional demand for aluminium by the turn of the century, which is in excess of the currently available capacity would be of the order of 440,000 tonnes per annum. Considering the payment for know-how, basic engineering and royalties for this additional follow-up stage this would mean an expenditure of at least US$ 95 million.

It is to be pointed out that the cost for Establishment of the Aluminium Centre in Nagpur (both Indian Government and UNDP contribution) is of the order of US$ 12.5 million. The financing of operations and further development of the Centre is envisaged by the Government to be secured through a collection of Rs. 100 per ton of aluminium for aluminium research and development, added to the price of aluminium (established now by the State in India). The funds so generated would serve as financial basis for operation and further extension of the Centre.

When the new aluminium capacity will be established the Centre will be fully functioning and if it contributes to savings of only ten per cent of the expected expenditure for project engineering and royalties, apart from rendering other useful services, its establishment would be fully justified.

It is to be noted that all the leading aluminium producing countries have their own R and D centres. Close interactions among these Centres' Research and educational institutions and industry has enabled numerous technological advances - this example is needed to be followed in India.

In the light of the above, a coordinated effort in R and D will be essential for the development of know-how and basic engineering to self-reliance in alumina and aluminium technology needed for the establishment of future plants without need to go for foreign consultancy. Future development of aluminium industry in the country based on indigenous expertise demands the immediate establishment of a self-reliance full-fledged and independent research, development and design centre for aluminium at the national level.

The development objective of the project is to aim at self-reliance in alumina and aluminium production technology and to achieve faster growth of the Indian aluminium industry to meet the domestic demand for aluminium products. This goal will be achieved by setting up of an Aluminium Research, Development and Design Centre at the national level which will be in a position to carry out research and development in the field of bauxite processing, alumina and aluminium production leading to improvement in the existing plants and creating new production facilities. Thus, the output of the project will be physical facilities of an Aluminium Research Development and Design Centre, adequately equipped with specialized research and testing equipment and trained professional staff to render research and development technology in the existing plants and for setting up of new alumina/aluminium production facilities based on indigenous raw materials and natural resources.

In addition, the Centre will handle related projects such as dealing with the use of by-products, design improvements for saving of energy and materials, development of new products and alloys. Another particular problem that the Centre is expected to address is emanating from the lack of adequate and uninterrupted power supplies which has led to poor utilization of capacities in the recent past. Investigations into energy saving technologies of alumina and aluminium production will be one of the important tasks that the Centre will have to tackle.

It is expected that once the Centre is established it will meet the fast growing technological service needs of the aluminium industry in India. The Centre will consist of the following departments:

- Alumina production research department with four laboratories and one pilot plant;
- Aluminium electrolysis research department with four laboratories;
- Analytical research department with three laboratories;
- General services, instrumentations and control department with four sections;
- General administration and finance department with three units.

The civil construction works for the Centre started in Nagpur in 1990 and will be finished by 1992-1993. The centre is planned to fully operate/function by 1994-1995.

The assignment of the national staff and procurement of equipment started in 1989-1990. The first R/D works have started in 1991-1992. Training of the staff is being carried out in India and abroad.

For a more detailed information reference could be made to the Project Document and the Detailed Centre Design.

JAWAHARLAL NEHRU ALUMINIUM RESEARCH DEVELOPMENT
AND DESIGN CENTRE, NAGPUR

NATURE AND ANALYSIS OF ORGANIC CONSTITUENTS IN BAYER CYCLE

DR. IBOLYA MOLNAR-PERL
UNIDO EXPERT

WORKSHOP
FEBRUARY 1, 1994

ANALYSIS OF ORGANICS PRESENT IN BAYER PROCESS

by Dr. Ibolya Molnar-Perl
UNIDO Expert, (Professor of Analytical Chemistry)
Sceme of lecture planned for the Workshop of February 1, 1994

Introduction:

Remarks, concerning the relevancy of the topic from the point of view of an analytical chemist also familiar with the difficulties of alumina plants.

Literary background:

a. Earlier suggestions for the quantitation of the total organic carbon contents
- by means of measuring the excess of the oxydation agents,
- by different calcination procedures, and,
- by wet oxydation methods.

b. Efforts in order to identify the composition of organics (mainly restricted to the analysis of aluminate liquor).
- quantitation of the total acidity of the eluate obtained by cation exchange procedure,
- separation of the organic constituents of the aluminate liquor by steam distillation; formic- and acetic acid determination in the destillate by means of selective methods).
- Estmation of the organics previously separated into three groups, i.e. fractions obtained by extractions performed
  - -- with ether (benzoic- and fenolic carboxylic acids),
  - -- with butyl alcohol (humic substances), and,
  - -- with cation echange ((formic-, acetic-, oxalic- and succinic acids).

Our achievements:

(Elaborated in the seventies, patented in 1978, supported by the Research Institute of FKI, Budapest, Hungary)

Basic principles in the development of our analysis system in order to determine the organics present in bauxites and in any other products originating from Bayer processes. (all kind of liquors, red mud, alumina hydrate, soda salt, etc.)

a, All groups of organics separated from the inorganic matrix on the basis of their physical or chemical properties were characterized

- as part of the total organic carbon content of the product
- by one or more selective analytical method qualitatively and quantitatively.

Thus, data obtained by the application of our selective analytical procedures are also given in organic carbon. By this, the possibility for establishing material balances and the easy handling and/or comparison of the experimental data was ensured, even in cases of different methods of analysis applying various matrices.

b. Qualitative and quantitative analysis of organics present in any products of alumina production, (further on: 'cycle organics') was performed both by classical and gas chromatographic mehods,

- mainly directly in the inorganic matrix without separation, or,
- subsequently to their isolation by distillation, steam distillation, intermittent or continuous liquid/liquid extraction etc.

c. This system of analysis is elaborated in such a manner that the groups of organics or individual organic substances, - being of primary importance from the point of view of alumina production, - can be determined with acceptable accuracy

- in the laboratories of plants on the one hand, and,
- they can also serve as a powerful tool in the analytical and technological basic researches aiming to solve the difficulties caused by organics in alumina production on the other hand.

d. Several hundreds of products originating from various alumina plants of all over the World have been analyzed by our system of analysis. Data obtained proved that:

e. 30-50 % of the 'cycle organics' is carboxy group,

f. their 80-100 % is carboxylic acid. It is to be emphasized that significant differencies exist in the relative amounts of the aliphatic-aromatic and humic acids, respectively depending on the bauxite and digestion conditions (temperature, pressure, alkali concentration) applied.

g. The elimination of the 'cycle organics' became projectable and can be folloved accordingly our analytical methods.

Data will be given in details as follows:

a. The principle of our total organic carbon determination method based on the bubble free distillation of CO_2. performed in 0.01 N scale, using potassium peroxy disulfate as oxydation agent catalyzed by silver sulfate.

The utilization of the total organic carbon measurement principle will be presented by

- Reproducibility studies given by the quantitation of 114-665 /ug organics present in different amounts of bauxites, red muds, alumina hydrates, aluminate liquors, etc.
- The essential characterization of the particle size of baxite to be analyzed for its organic content will be shown by bauxites of various origine.
- Organic balances taken in closed Bayer cycles with Hungarian and Koyna bauxites.

b. The principle of our direct esterification method, - carried out in the presence of the inorganic matrix by the use of sulfuric acid/n-butanol as esterifying agent -

- providing the n-butyl esters of quite all carboxylic acids present in 'cycle organics'
- representing the 80-95 % of the total organic carbon of products in alumina production,
- determined gas chromatographically from one solution by one injection.

c. Determination of the humic acid contents.

d. Additional methods, such as continuous liquid/liquid extraction, amino Nitrogen determination, etc

Chriticism of our methods also in comparison to those presented recently in the literature (restricted for the analysis of solutions), such as

- HPLC,
- GC/MS

NATURE AND ANALYSIS OF ORGANIC CONSTITUENTS IN THE BAYER CYCLE

I. MOLNAR - PERL

Introductory remarks

Required characteristics of analytical system proper to control and influence the damage done by organic materials entering the Bayer cycles. This complex and exact analysis system should furnish

- reliable, reproducible and "acceptably" accurate data.
- concerning the quantity and the quality of the organics equally. Satisfactory to determine all of those organics present
- in very different amounts 10^{-5} - 30 %,
- in inorganic matrices of basically different composition, and
- in completely various oxydation stages : present
- in dissolved form (aluminate liquors, soda salts, alumina hydrates), or,
- in mainly "undissolved conditions" (bauxites, red muds)

The oxydation stage of organics increases, in order of listing:

kerogens
humic substances
humic acids
fulvic acids
aliphatic and aromatic mono-, di and polycarboxylic acids.

- The system should be applicable both for routine duties, and research works, and, finally
- it should be achievable for a reasonable price .

CLASSIFICATIONS OF METHODS OF OUR ANALYSIS SYSTEM

Methods of primary importance (exclusively our principles)

- The total organic carbon measurement based on the bubble free distillation of CO_2 obtained from the oxydation of organic compounds by potassium peroxy disulfate catalyzed by silver ions [1,2].
- The quatitation of humic acids based on the measurement of their total organic carbon content.
- The quantitative and qualitative determination of all dissolvable carboxylic acids, esterified directly in water containing solutions, in the presence of the inorganic matrix by sulphuric acid/n-butanol prior to their quantitation by gas chromatography: from one solution by one injection. This principle [3-19] covers approximately 80-100% of dissolved organic constituents, present in any inorganic matrix, in dissolved conditions.

Methods of particular importance in sophisticated researches.

Isolation of organic compounds from the inorganic matrix

- by continuous solid/liquid and/or liquid /liquid extraction prior to or/and after digestion providing

  in the case of undigested bauxites the neutral organics, such as n-paraffins, aliphatic fatty acids of long chain, etc., maximum 2 % of the total oganic content,

  in the case of dissolved organics relating to all carboxylic acids (including the sterically hindered carboxylic groups, having four or more carboxy groups on the neighbouring C atom of the aromatic ring.
- by distillation combined with hypochlorite oxydation in order to determine the total amino-nitrogen content of liquors and soda salts,
- by steam distillation directly from the acidified inorganic matrix resulting in three fractions, such as volatile organics, humic acids, and the non volatile fraction.

METHODS OF TOTAL ORGANIC CARBON MEASUREMENTS

Literary background [20-31]

- Measuring the excess of the oxydation agents proposed first to the quantitation of organics present in water: insufficient indicating the 10-40 % of the actually present organics only.
- Calcination procedures widespread used in soil and rock analysis; time consuming, tedious principles resulting in lost of volatiles.
- Wet oxydation procedures; shortages of earlier proposals:
    - -- unsuitable apparatus,
    - -- incorrectly choosen oxydation agents,
    - -- methodological inadequacies,
    - -- lack of quantitative removal of carbonates maintaining the quantiative intactness and retention of the volatile organic compounds, simultaneously ;

Our principle

Bubble free distillation of CO_2 [1, 2, 38-40]

- First application in 0.1 N scale proper to plant liquors exclusively.
- The extension of the method, for bauxites and for all of its digestion products, needed exhaustive basic research, performed as a function
- of the quantity and quality of organic compounds to be oxydized in competition with the mineral cabonates to be eliminated ,
- of the quantity and quality of the oxydation agent to be applied, and,
- of the optimum time requirements of the CO_2 elimination and oxydation steps, equally.

The importance of the 0.01 N scale of measurements :

- All requirements can be fulfilled in micro-dimension exclusively; i.e., the quantitative CO_2 elimination, combined with the transformation of organics even present in low oxydation stages into the maximally oxydizable condition without any loss.

The removal of CO_2

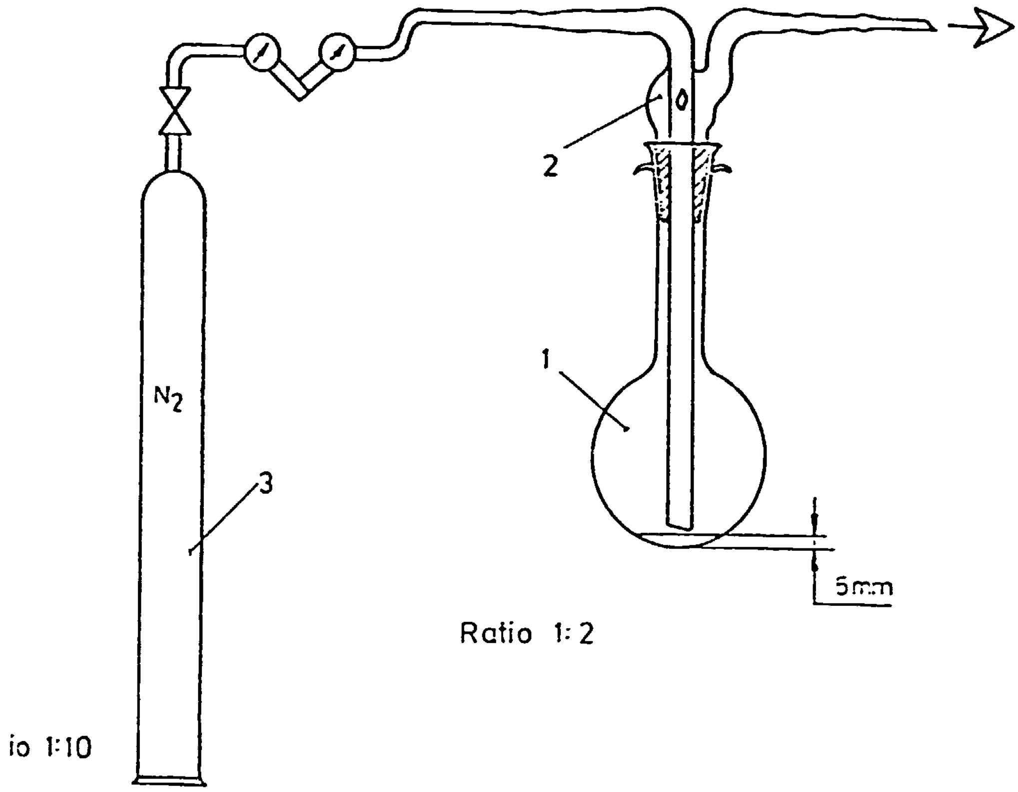
- dependent of the physical and chemical characteristics of the matrix and the organics to be determined, i.e. it is to be carried out differently
- by bubbling of high purity nitrogen through the acidified solutions for dissolved organics, such as liquors, soda salts (Fig. 1), or,
- refluxing the acidified heterogeneous matrix of bauxites and red muds performing CO_2 elimination and digestion simultaneously (Fig. 2)
- Short survey of the procedure (Fig. 3).

Reproducibility studies : (100 - 600 /ug organic carbon)

- Obtained by dissolved organics (Table 1), characterized by the relative standard deviation (RSD) percentages <2.5%
- Experiences by the quantitation of partly dissolved organic constituents: the importance of the pulverization degree of bauxites and red muds (Table2).
- Obtained by partly dissolved organics, present in the lower oxidation stage, performing optimum conditions (Table 3, RSD , <6%).

Fig. 1.

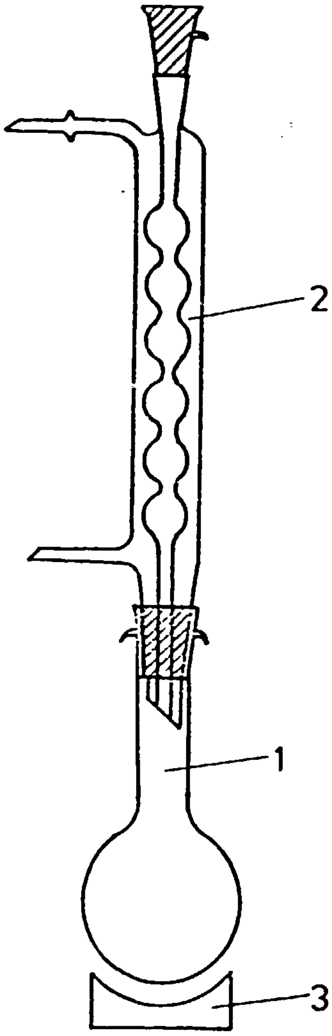
APPARATUS FOR THE ELIMINATION OF THE CARBON DIOXIDE CONTENT FROM ALUMINATE LIQUOR AND SODA SALT SAMPLES



1. Spherical flask
2. Gas inlet pipe
3. N_2 gas cylinder with reducer

Fig. 2.

APPARATUS FOR THE ELIMINATION OF THE CARBON DIOXIDE CONTENT FROM BAUXITE, RED MUD AND ALUMINA HYDRATE SAMPLES

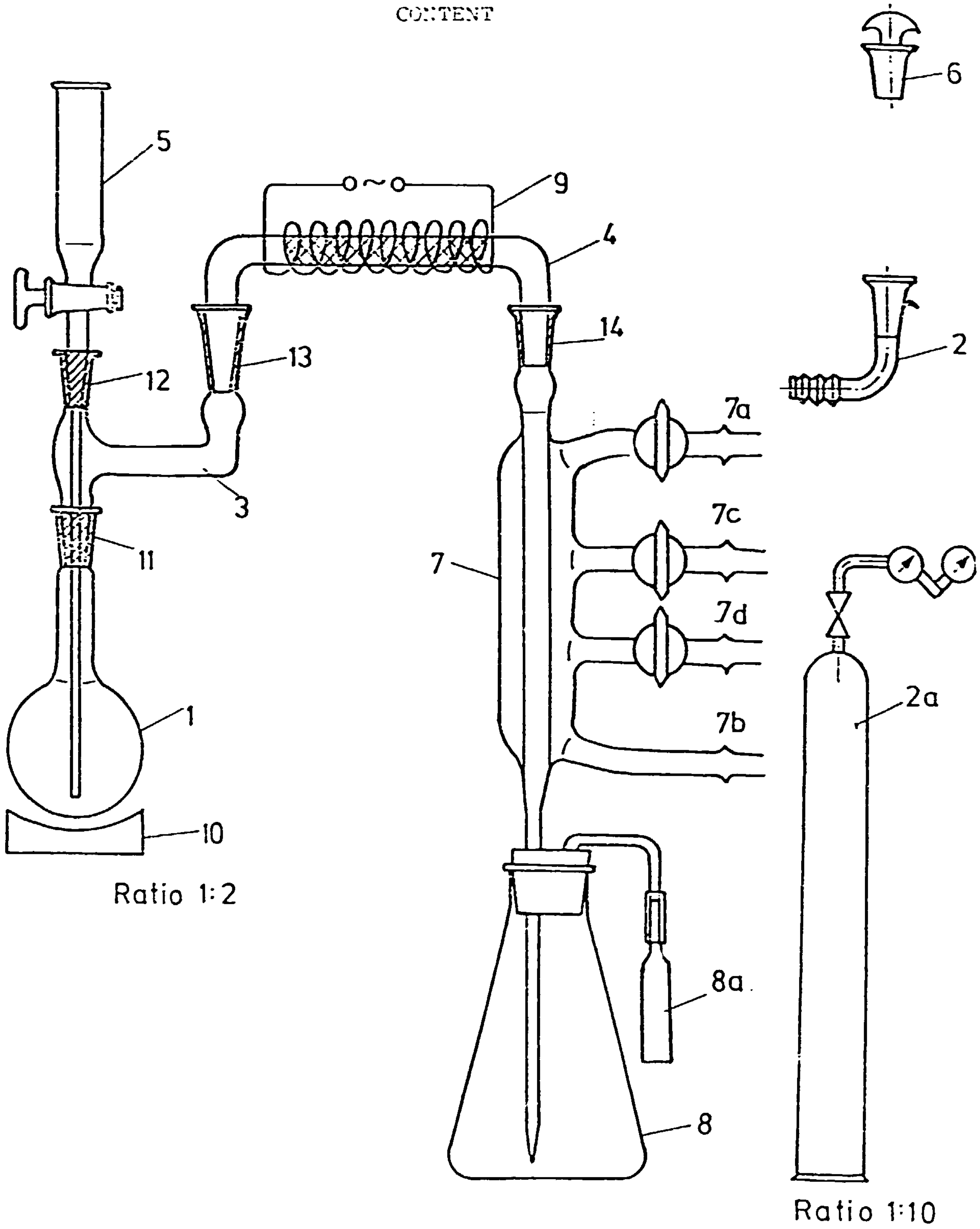


Ratio 1: 2.5

1. Spherical flask
2. Glass condenser
3. Hot plate

Fig. 3.

APPARATUS FOR DETERMINATION OF THE TOTAL ORGANIC CARBON CONTENT



1. Spherical flask
2. H_2 gas inlet pipe
2a. H_2 gas cylinder with reducer
3. Distributing pipe
4. Quartz pipe filled with copper wire
5. Feed funnel
6. Glass stopper
7. Cooler with water connections (7a, 7b, 7c, 7d)
8. Carbon dioxide absorption flask
8a. Glass tube filled with soda asbestos
9. Heating coil
10. Electric heater
11 to 14. Ground joints

Table 1

Determination of the total organic carbon content of plant liquors

Plant liquor weighed cm^3/cm^3	Solution weighed cm^3	0.01 N HCl consumed cm^3		Organic carbon found g/dm^3		
		singly	mean value	mg	singly	mean value
Plant liquor$_1$ 10,00/1000,0	10,00	10,97 11,03 11,08	11,03	0,662	6,62	
	4,98	5,73 5,57 5,67	5,66	0,340	6,83	6,66 S.D. = 0,16 R.S.D.%= 2,4
	2,01	2,07 2,23 2,26	2,19	0,131	6,52	
Plant liquor$_2$ 10,00/1500,0	10,00	10,37 10,34 10,34	10,35	0,621	9,31	
	4,98	5,20 4,94 5,18	5,06	0,304	9,16	9,19 S.D. = 0,1 R.S.D.%= 1,0
	2,01	2,07 1,96 2,09	2,04	0,122	9,11	

S.D. = Standard Deviation
R.S.D.% = Relative Standard Deviation %

Table 2

Total carbon content of bauxite samples as a function of pulverisation degree

Sieve: mesh mm	Organic carbon 10^{-2} g/100 g air dry bauxite									
	$Bauxit_1$		$Bauxit_2$		$Bauxit_3$		$Bauxit_4$		Bauxit	
	singly	mean value	singly	mean value	singly	mean value	singly	mean value	singly	mean valu
0,16	6,30 5,70 6,00	6,0	6,14 6,07	6,1	14,6 14,5 14,1	14,4	6,90 6,60	6,8	3,75 4,21	4,0
0,08	6,60 6,70	6,70	6,97 7,30	7,1	14,4 15,1	14,8				
0,063	7,13 7,10	7,1	4,34 7,80	7,6						
0,050	7,97 7,40 7,73	7,70 S.D. =0,29 R.S.D.%=3,7	7,93 7,64 7,50 7,76	7,70 S.D. =0,17 R.S.D.%=2,2	14,3 14,4	14,4	7,00 6,70	6,9	4,77 4,82	4,8
	$Bauxit_6$		$Bauxit_7$		$Bauxit_8$		$Bauxit_9$		$Bauxit_{10}$	
0,16	20,2 20,3 20,3	20,3 S.D. =0,58 R.S.D.%=2,8	16,8 17,0 16,4	16,7 S.D. =0,30 R.S.D.%=1,8	8,57 9,12 8,46	8,7	27,6 28,7	28,2	7,70 7,91	7,8
0,050	20,9 20,8 20,3 20,5	20,6 S.D. =0,28 R.S.D.%=1,3	18,4 18,7 18,4	18,5 S.D. =0,17 R.S.D.%=0,94	8,66 9,02 8,35 9,16	8,8 S.D. =0,37 R.S.D.%=4,1	28,6 28,7	28,7	8,24 8,54 8,15	8,3 S.D. =0,20 R.S.D.%=2,4

S.D. = Standard Deviation
R.S.D.% Relative Standard Deviation %

Table 3

Total organic carbon content of bauxites* red muds and alumina hydrates from different measurements
/* air-dry samples ground below 0.05 mm particle size/

Sample	Amount of bauxit taken g	0.01 N consumed cm^3	Organic carbon found mg	Organic carbon found 10^{-2} g/100 g bauxit singly	Organic carbon found 10^{-2} g/100 g bauxit mean value
Bauxit$_1$	0,3267	4,06	0,244	7,45	7,71 S.D. =0,30 R.S.D.%=3,8
	0,4803	6,40	0,384	7,92	
	0,5000	6,64	0,398	7,97	
	0,5504	7,09	0,425	7,73	
	0,5909	7,27	0,436	7,38	
	0,6141	7,82	0,469	7,64	
	0,6690	9,13	0,548	8,19	
	0,8420	10,40	0,624	7,41	
Bauxit$_2$	0,2916	3,59	0,215	7,39	7,66 S.D. =0,40 R.S.D.%=5,2
	0,2888	4,18	0,251	8,40	
	0,6910	9,13	0,548	7,93	
	0,8846	11,43	0,686	7,75	
	0,9756	12,42	0,745	7,64	
	1,0204	12,67	0,760	7,45	
Bauxit$_3$	0,1612	4,04	0,242	15,0	14,40 S.D. =0,51 R.S.D.%=3,5
	0,1632	4,04	0,242	14,4	
	0,3344	7,79	0,467	14,0	
	0,3414	8,10	0,486	14,2	
	0,5164	12,92	0,775	15,0	
	0,6514	14,94	0,896	13,8	

Sample	Amount of redmud or alumina hydr. taken g	0,01 N HCl consumed cm^3	Organic carbon found mg	Organic carbon found 10^{-2} g/100 g re mud or allm. hidr. singly	Organic carbon found 10^{-2} g/100 g re mud or allm. hidr. mean value
Red mud$_1$	0,1293	1,90	0,114	8,84	8,33 S.D. =0,30 R.S.D.%=4,7
	0,3082	4,24	0,255	8,26	
	0,4660	6,82	0,409	8,78	
	0,4697	6,21	0,372	7,93	
	0,5161	6,95	0,417	8,08	
	0,6018	8,09	0,486	8,07	
Red mud$_2$	0,4982	6,21	0,372	7,47	7,20 S.D. =0,30 R.S.D.%=4,2
	0,5768	6,70	0,403	6,88	
	0,6170	8,14	0,488	7,27	
Red mud$_3$	0,1855	5,34	0,320	17,3	17,40 S.D. =0,95 R.S.D.%=5,5
	0,1858	5,71	0,342	18,4	
	0,2478	6,82	0,409	16,5	
Alumina hydrate$_1$	5,800	2,02	0,121	2,08	2,10
	5,536	2,00	0,120	2,17	
Alumina hydrate$_2$	5,603	3,45	0,207	3,69	3,60
	5,226	3,02	0,181	3,46	
Alumina hydrate$_3$	0,0795	5,22	0,313	39,4	40,0
	0,0982	6,65	0,399	40,6	

S.D. and R.S.D.% as in Tables 1 and 2.

Utilizations of the total organic carbon quantitation method.

Literary background [24, 25, 32-34]

- The first trial [32] was done in parallel with calcined and uncalcined bauxites in 11 and 12 closed Bayer cycles, respectively. Due to the insufficient method used, (measuring the excess of MnO_4^-), after the 5. and 6. cycles saturation level has been found: 0.028 and 0.07 organic C/l respectively.

- Hungarian researchers [24, 25] tried to measure the dissolution of organics in one cycle into the plant liquor: the difference resulting in the dissolution in a single cycle could not be measurered.

- Schepers [33], reported 48 % digestion of native organics. If it would be so, this organic problem would not exist in alumina production
- Jamada's [34] results done in Sumitomo Chemical Co-Laboratories proved to be in accordance with ours.

Our studies

Model organic carbon balances, performed in closed Bayer cycles. One of the most important application of this technique.

- Applying three different bauxites in 6, 5 and 2 closed Bayer cycles, without sedimentation agent, - with one out of the three, - also in parallel, in 5 cycles, using rye-flour as flocullant.
-- Following throughly the conditions of the given plant descriptions in any terms,
-- assuring the completely 'organic contaminants free' conditions synthetic aluminate liquor, alumina hydrate prepared from synthetic aluminate liquor).

- Bauxites and every products of its digestion have been analyzed by those reproducibility values given in Tables 1-3.

Organic carbon balances

- Taken in 6 Bayer cycles without sedimentation agent. Bauxite: Halimba, Hungary. Organic carbon content 7.70 x 10^{-2} g /100 g (Table 4).

- Taken in 5 Bayer cycles, applying 2.5 g rye flour/ 1000g Halimba Halimba bauxite (Table 5).

- Taken in 2 Bayer cycles (the first cycle in parallel) without sedimentation agent. Bauxite: Koyna, India. Organic carbon content 14.8 x 10^{-2} g/100 g bauxite (Table 6).

Data evaluation of organic carbon balances of model cycles defined

- by the amount of organics dissolved into the aluminate liquor in the given cycle.

- by differences between input and output of organics i.e. by the degree of degradation

- by the organic contents of red muds, aluminate liquors and aluminate hydrates in every subsequent cycle, and ,

- the distribution of organics remaining and leaving the cycles, as well comparison of data provided by three different bauxites (Table 7).

Table 4

Organic balance of Halimba bauxite /Hungary/ in 6 Bayer cycles

In the 1st cycle there was 936 g bauxite digested, having organic content of 4,80.10^{-2} g organic carbon/100 g bauxite. In the 2-6 cycles there was 900 g bauxite digested per cycles, with organic content 7,7.10^{-2} organic carbon/100 g bauxite

Number of the cyclo		Organic carbon g							
		with bauxite	with aluminate liquor	with alumina	with red mud	with washing liquor of red mud	total	difference % x1	x2
1. vaporation	in	0,461	0,042	0,024			0,527		0,166
	out		0,190	0,059	0,207	0,018	0,474	- 10,0	
2. vaporation	in	0,693	0,205	0,026			0,924		0,252
	out		0,411	0,032	0,385	0,046	0,874	- 5,4	
3. vaporation	in	0,693	0,443	0,020			1,156		0,226
	out		0,575	0,062	0,393	0,094	1,124	- 2,8	
4. vaporation	in	0,693	0,660	0,034			1,397		0,169
	out		0,717	0,052	0,476	0,122	1,367	+ 3,0	
5. vaporation	in	0,693	0,831	0,028			1,552		0,123
	out		0,830	0,068	0,472	0,123	1,493	- 3,8	
6. vaporation	in	0,693	0,958	0,039			1,690		0,281
	out		1,062	0,072	0,406	0,177	1,717	+ 1,7	
					1,239 (31,6 %)				

recipitation of soda salt	0.821 g /67.8 %/ /in 2060 ml strong liquor/ C: 0.399 g/l	0.390 g /32.2 %/ /in 697 g soda salt/ C: 0.0559 g/100g

x1: total error of technological and analytical experiments, in this case and during every digestion

x2: dissolved into the aluminate liquor in the given cycle

Table 5

Organic balance of Hungarian Halimba bauxite in 5 Bayer cycles sedimentation promoted with rye-flour

900 g bauxite digested per cycle, organic content: $7,7.10^{-2}$ g organic carbon/100 g bauxite 2.25 g rye-flour, measured by analytical precision was added per cycle for sedimentation, having organic content of 0.383 g organic carbon/g rye-flour

Number of cycle		Organic carbon g								
		with bauxite	with rye-flour	with aluminate liquor	with alumina hydrate	with red mud	with vashing liquor of red mud	total	difference % x1	x2
1. evaporation	in	0.693	0.862	0.024	0.023			1.602	+ 0.9	0.475
	out			0.429	0.086	1.032	0.070	1.617		
2. evaporation	in	0.693	0.866	0.482	0.044			2.085	- 5.2	0.377
	out			0.753	0.097	1.024	0.102	1.976		
3. evaporation	in	0.693	0.862	0.852	0.048			2.455	- 1.4	0.453
	out			1.114	0.083	1.033	0.161	2.421		
4. evaporation	in	0.693	0.864	1.304	0.042			2.903	+ 4.3	0.509
	out			1.610	0.101	1.114	0.203	3.028		
5. evaporation	in	0.693	0.866	1.698	0.054			3.308	- 4.8	0.342
	out			1.705	0.069	1.120	0.255	3.149		

1.960 (25.2 %)

Na-salt precipitation

1.465 g /74.1 %/ /in 2200 ml strong liquor/ C: 0.665 g/l	0.512 g /25.9 %/ /in 555 g Na-salt/ C: 0.0923 g/100 g

x1 and x2 of. Table 4

Table 6

Organic balance of Koyna bauxite /India/ in 2 Bayer cycles

In the two 1st cycles 550 g, in the 2nd cycle 775 g bauxite were digested, having organic content of $1,48.10^{-1}$ g organic carbon/100 g bauxite
The two 1st cycles show the reproducibility of technological and analytical experiments.

Number of the cycle		Organic carbon g							
		with bauxite	with aluminate liquor	with red mud	with washing liquor of red mud	with alumina hydrate	total	difference % x1	x2
1/a evaporation	in	0.814	0.020			0.036	0.870	- 4.0	0.638
	out		0.629	0.132	0.029	0.045	0.835		
1/b evaporation	in	0.814	0.027			0.030	0.871	- 1.0	0.636
	out		0.634	0.154	0.029	0.045	0.862		
2/b evaporation	in	1.150	0.594			0.032	1.776	- 2.1	0.802
	out		1.330	0.264	0.066	0.078	1.738		

1.305 g (65.5 %)

/in 3000 ml strong liquor/
C: 0.435 g/l

x1 and x2: as in Table 4 and Table 5.

Table 7

Final organic balance of digestion series made of different bauxite without the use of sedimentation promoting agent

Total during digestion	Organic carbon					
	From Halimba bauxite /Hungary/ in 6 Bayer cycles		From Iszkaszentgyörgy bauxite /Hungarian/ in 5 Bayer cycles		From Koyna bauxi /India/ in 2 Bay cycles x2	
	g	%	g	%	g	%
In	3.992	100.0	2.682	100.0	2.021	100.0
In aluminate liquor	0.821	20.6	1.490	55.6	1.305	64.6
In soda salt	0.390	9.8	0.015	0.6	0.0	0.0
In red mud	2.339	58.6	1.070	39.9	0.418	20.7
In product hydrate	0.198	5.0	0.110	4.1	0.091	4.5
Degraded	0.174	4.3	can not be x1		0.182	9.5
Used for the analysis	0.070	1.7	0.055	2.1	0.015	0.7

x1: As it is evident from the results of Table 2, the 2nd cycle of thi serie was contaminated during the decomposition of alcali with organics, 0.12 g expressed in terms of organic carbon. However in this digestion serie the quantity of degradation could not have been evaluated.

x2: Evaluated from the data of the 1/b and 2/b cycles of Table 3.

WHAT ABOUT THE EXPECTED SATURATION LEVEL OF ORGANICS WHEN OPENING A NEW BAUXITE BLOCK

- Can it be judged ? yes or not ? The answer is yes,

Comments :

- Accordingly our results in accordance with those reported by Jamada [34] it became evident :

- because of the tedious and time consuming analytical and technical investigations,

- both the dissolution of organics into the Bayer cycle and their leaving the system, - in limited number of cycles, - proved to be quasi linear .

- Thus, by some model cycles neither the equilibrium organic level, can be obtained nor the number of actual, real cycles reaching to this can be calculated. Therefore we introduced

The term of the 'theoretical number of Bayer cycle' based on our own experimental data in accordance with those reported by Jamada (Table 8).

In order to get the judged saturation level of aluminate liquor prepared from a newly opened block, only, the experimental organic carbon content of aluminate liquor obtained in one model Bayer cycle should be defined and multiplied by 40 .

Table 8

Figures of theoretical number of cycles calculated from the organic carbon content of liquors of model cycles and plants and from literature data

Bauxite	Temperature of digestion °C	Total organic content of bauxite g/100 g	Dissolved organics %	Organic carbon content of aluminate liquor g/l		Theoretical number of cycles	
				During 1 Bayer cycle	In plants after when Bayer cycles were conducted to saturation	By each	Mean value
Calculated from our own experiments							
Halimba a.	220	0.077	21	0.072	5.02	69.7 /34.8/[x]	39.6
b.	220	0.077	19	0.133	5.02	37.7	
Koyna	140	0.161	61	0.217	10.40	47.9	
Weipa	220	0.185	75	0.386	14.70	38.1	
Calculated from experimental results obtained by Yamada[20]							
South-East Asia	150	0.16	74	0.201	8.1	40.3	37.7
Australia /1/	150	0.36	69	0.447	17.1	38.3	
	230		75	0.485	-		
Australia /2/	150	0.25	69	0.310	-		
	230		78	0.351	11.3	32.2	
Island	150	0.49	74	0.617	24.6	39.9	
Africa	150	0.13	72	0.168	5.5	32.7	
	230		80	0.870	-		

a: in cycles without the use of sedimentation promoting agent

b: in cycles when rye-flour was used to promote sedimentation

x: value calculated the way that native and sedimentation promoting agent organics entering the cycle are considered to dissolve in equal portions.

Table 9.
Organic balances of 'Balco'(46 g) and 'Nalco'(55 g) bauxites, taken in 1 Bayer cycle, digested of each by 120 ml synthetic aluminate liquor, at plant conditions.

BAUXITE CYCLE	BAUXITE	ALUM. LIQU	RED MUD	WASHING SODA	TOTAL	DISSOL -VED	%
`BALCO'I IN	0.0415	0.0048			0.0463		
OUT		0.0293	0.00809	0.00547	0.0428	0.0348	75
`NALCO' Ia IN	0.0239	0.0048			0.0287		
OUT		0.0193		0.00397		0.0233	81
`NALCO' Ib IN	0.0239	0.0048			0.0287		
OUT		0.0194		0.0308		0.0224	78

TOTAL ORGANIC CARBON OF :

1.) BAUXITE g. / 100 g.

SOURCE	SINGLE	MEAN	R.S.D. %
BALCO	0.0921 0.0898 0.0945 0.0883	0.0902	4.3
NALCO	0.0409 0.0433 0.0463	0.0435	6.2

2.) SYNTHETIC ALUMINATE LIQUOR TAKEN FROM 4 BOMBS g. / l.

SINGLE	MEAN	R.S.D. %
0.044 0.042 0.036 0.045	0.042	9.6

THE QUANTITATION OF HUMIC ACIDS

Literary background

Humic acids centred view [26, 28, 30, 32, 33] : due to their spectacular physical characteristic, i.e., they are

- highly soluble in alkalines,
- insoluble in acids.

Consequently their presence can be judged quite as good macroscopically as by UV spectrophotometry method, proposed and commonly used for their quantitation.

Spectrophotometric procedures, - based on the measurement of their absorbances in the UV region of 380 -420 nm, - can be classified accordingly their time consume and cost : performed

- with the alkaline liquors directly,
- by the isolated humic acid, previously precipitated, filtered, then dissolved in alkalines, and,
- by their fractions, differentiated accordingly their molecular weight applying gel permeation chromatography.

Comments : All the quantitation methods based finally on the measurement of the absorbance of their alkaline solutions are leading to the same results. These results are not comparable because the absorbance characteristics of humic acids are dependent

- on the quality of the bauxite they have been formed from , and,
- on the condition of digestion parameters applied in the given plants.

Conclusion: A comparable humic acid quantitation method was needed.

HUMIC ACID QUANTITATION BY OUR PRINCIPLE

Based on the total organic carbon quantitation of the isolated humic acids

- Requirements: quantitative isolation, and,
  quantitative oxydation.

- Results: optimum conditions have been achieved as a result of our exhaustive basic study performed with a number of humic acids of different origin, performed

  -- by different amounts of humic acids,
  -- stored for various time after precipitation,
  -- in different series.

- Reproducibility: (Table 10) proved to be the same as given by the total
  organic carbon measurements (characterised by their R.S.D. %)

- The completion of the method is simple:
  -- sample are to be weighed in by analytical accuracy into a baker,
  -- acidified by 10 - 20 ml of 40 % H_2SO_4 (mixed by glass rod),
  -- stored for >4 h,
  -- filtered on glass filter paper, washed until the eluent reaches pH < 3,
  -- dissolved the humic acids by 1 N NaOH into a measuring flask, and,
  -- determined an aliquot of their alkaline stock solution through their
  -- total organic carbon contents.

Table 10

Humic acid content of aluminate liquor after precipitation with sulfuric acid

Amounts used for analysis		Storage time of precipitated humic acid hrs.		Amount of precipitated humic acid %		
Aluminate liquor$_1$ cm^3	40 % H_2SO_4 cm^3			a	b	
5.00	10	4		3.6	3.6	
5.00	10	48	Mean=3.48	3.4	3.7	3.58
10.00	20	4	S.D. =0.095 R.S.D.%=2.8	3.5	3.5	0.096 2.7
10.00	20	24		3.4	3.5	

% expressed in the percentage of the total organic carbon

a and b: parallel measurements.

THE QUALITATIVE AND QUANTITATIVE DETERMINATION OF ORGANIC CONSTITUENTS

It is to be focused on the two main types of organics, it means

- on the not dissolved or partly dissolved organic materials present in relatively low oxydation stage

  - in bauxites before digestion, and ,
  - in red muds after digestion (further on: 'bauxite organics', and,

- on the dissolved organics, present in relatively high oxydation stage, in liquors, soda salts and alumina hydrates, originating both from bauxites and from those of flocculating agents (henceforth: 'cycle organics').

Literary background

'Bauxite organics': At the start of our work no literature data could be found ; methods commonly used for the analysis of rocks (mainly shale rocks) and sediments were unsuitable for the analysis of bauxite organics.

'Cycle organics': works relating mainly to the investigations of aluminate liquors can be characterised by their partial nature, it means they do not strike to make material balances dealing mainly with

- humic acids [20-28, 30, 31, 33-36].

- Shehyn [41] titrated the total acidity of the cation exchanged aluminate liquors, decreasing this value by the mineral acid contents of eluate followed by their quantiation applying gravimetric methods.

- Lever [42] divided the organic materials of aluminate liquor into three groups by extractions assuming that
  - -- in the extracts obtained by n-butanol the humic acids, while
  - -- in the ethereal extract the benzoic- and phenolic acids can be isolated: being completely unfamiliar with their distribution coefficients in any of solvents. Recently,

- the HPLC (high performance liquid chromatography) technique was also tried to utilise for the analysis of aluminate liquors; this technique proved to be of secondary importance from the point of view of practice. Reasons: the insufficient separation of acids and its high cost.

- The GC/MS (gas chromatography/mass spectrometry), utilized for research purposes concerning the analysis of aluminate liquors only.

- The IC (ion chromatography) relatively common in alumina plants, proved to be an important tool in the analysis of inorganic anions, and in addition it can be also used in the determination of organic anions of low molecular weight.

Our principle

Based on the qualitative and quantitative determination of all dissolvable carboxylic acids about the 80 - 100 % of total organic carbon present (excluding the sterically hindered aromatic polycarboxylic acids, i.e. the 0-20 % of the total).

- Esterified quantitatively, directly in water containing solutions,
- in the presence of the inorganic matrix (relating also to bauxites and to all of its digestion products),
- by sulphuric acid /n-butanol,
- indentified and quantitated by gas chromatography,
- more than 20 components, from formic acid to pyromellitic acid,
- from one solution by one injection (followed the extraction of esters by chloroform).

Principle of esterification

As a result of a really exhaustive basic research [2-19] performed with all possibly homologous series of carboxylic acids being represented by their chosen members in 'cycle organics', we could prove that

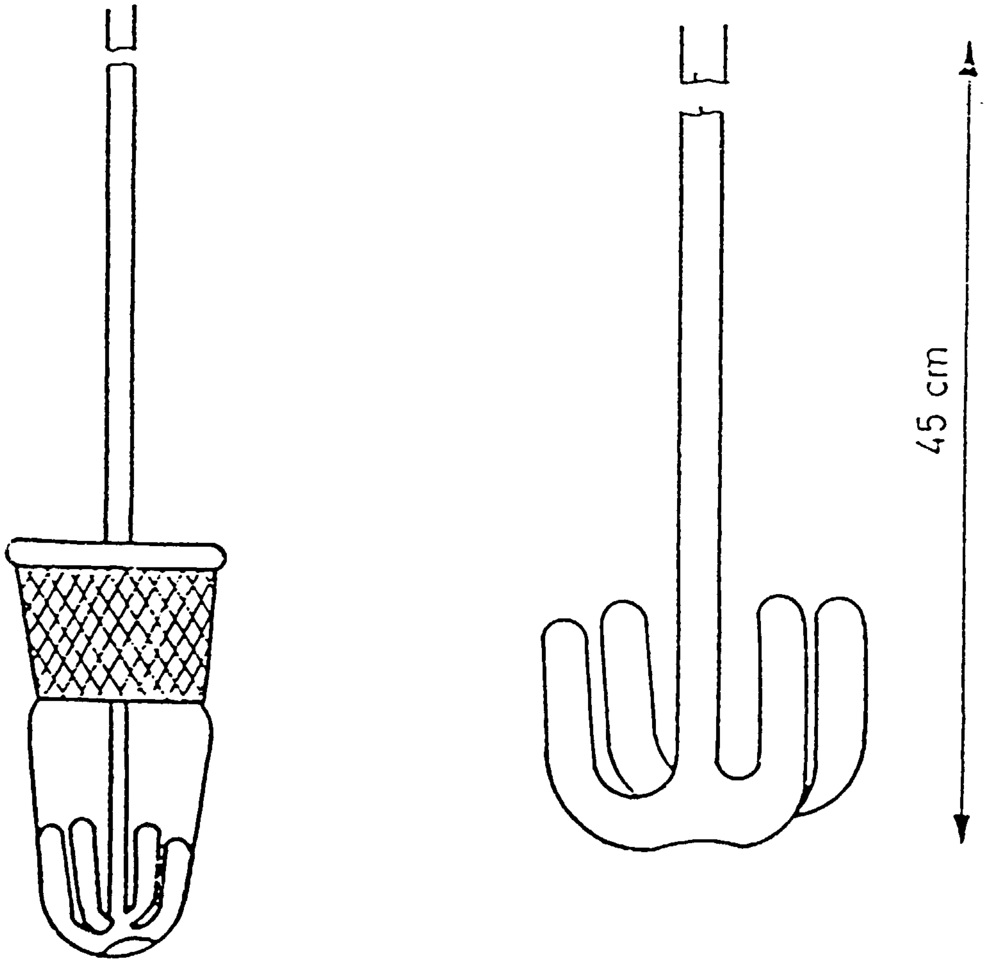
- taking the water containing solution of acids,
- in the presence of a given amount of anhydrous sodium sulfate,
- by means of sulphuric acid / n-butyl alcohol,
- quantitative esterification yield can be achieved.

This phenomenon can be explained by the fact that under esterification condition the water content of the system will be transformed to the crystal water of sodium sulfate forming mainly sodium sulfate decahydrate.

In the case of aluminate liquors by mixing them with n-butanol in the presence of cc sulphuric acid, under neutralization reaction, the same process takes place, i.e., sodium sulfate decahydrate is formed decreasing the water content of the system to that extent resulting in the quantitative esterification yield of the above mentioned organic acids present.

Fig. 4.

BUTYLESTERIFYING VESSEL AND STIRRER



Ratio 1:2

Ratio 1:1

COMPLETION OF THE METHOD

- Esterification:
  Exclusively n-butyl alcohol proved to be suitable as esterification agent because of the very simple fact that the boiling point of any other alcohol is so close to the boiling points of the corresponding formic acid esters that their separation could not be achieved.

- Apparatus: I designed a very simple glass assembly for this special purpose. It consists of a special esterification flask of a relatively wide neck with a ground joint fittable to the reflux condenser and as well to the vacuum rotary evaporator (Fig. 4).
- Isolation of the n-butyl esters by extraction with chloroform and the evaporation of the extract in order to get the stock solution of esters suitable for

- separation and subsequent quantitation of the esters by gas chromatography;

- Gas chromatographic conditions:
  - high separation efficiency was needed providing the separation and quantitation of esters of different members of various homologous series of carboxylic acids, from formic acid to polycarboxylic acids from one solution by one injection .
  - Out of the wide choice of column coating materials only Dexsil provided this high separation capacity (Figure 5).

- Evaluation of the componets using external standards, certainly expressing their amounts in organic carbon, as a part of the total organic carbon content of the given sample.

Practical utilisation

Suitable for the quantitation of the overwhelming part of carboxylic acids present in any sample of alumina production (80-100 % of the total organic carbon)

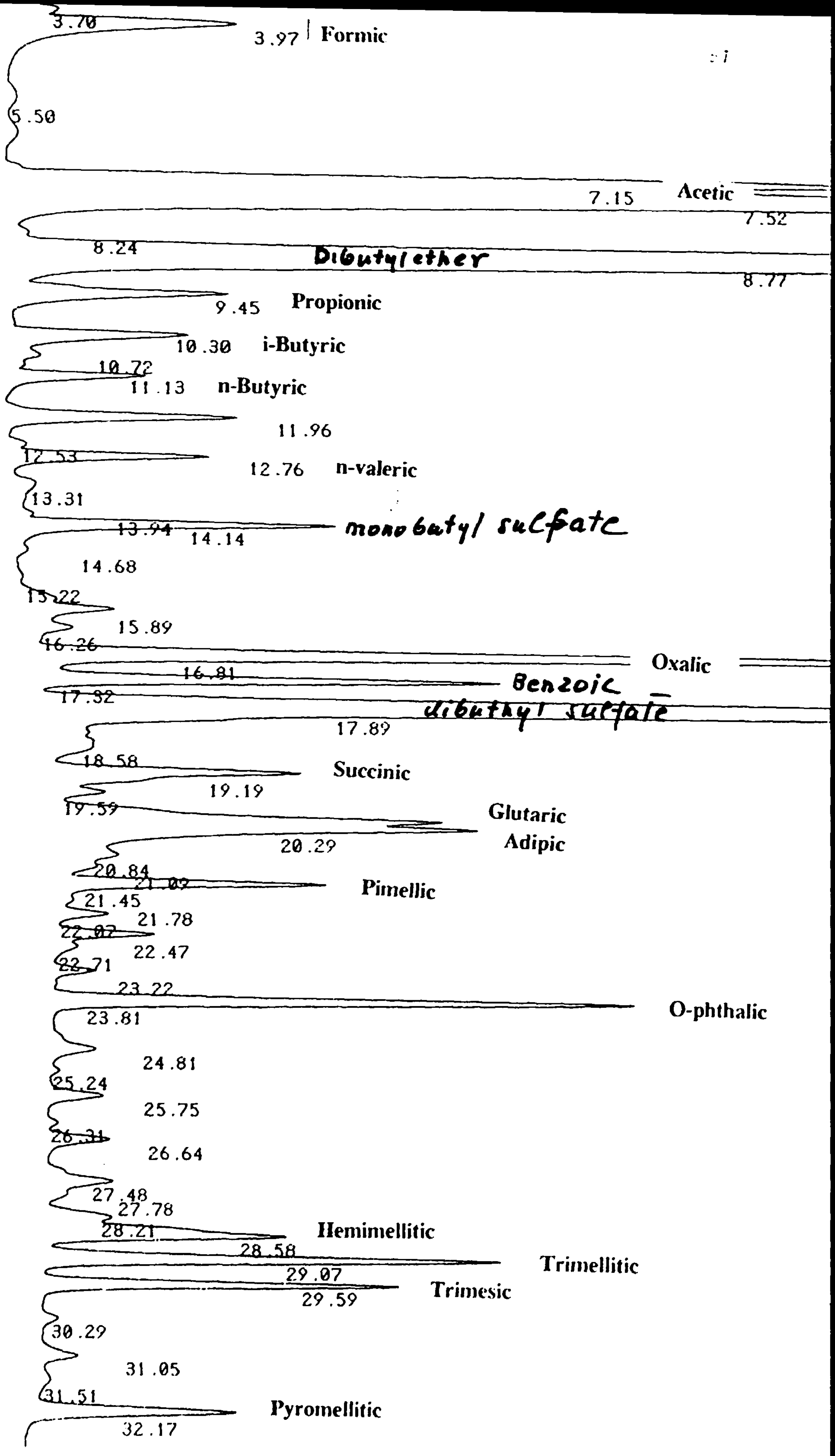


Fig. 1 Chromatogram of n-butyl esters of a model solution (taken in the JNARDDC, Nagpur)

Composition of selected samples containing cycle organics (Table 11)

- Values expressed in percentages of the total organic carbon content of the samples proved that
  - humic acids are exclusively of natural,
  - amino acids are primarily of rye flour origin,
  - the low molecular weight members of the fatty acid series are originating from both sources, quite equally,
  - oxalic acid is coming also from the both sides. Regarding the distribution of its origin it depends on the characteristics of bauxites applied.
  - The aromatic polycarboxylic acids, certainly are originating from bauxites exclusively.

As to the identification percentages, (when the amount of the sterically hindered aromatic polycarboxylic acids can be neglected),

- in cases of plant products of a total organic carbon content of > 1 g/l (1 g/1000g) can reach the hundred percent, while,
- in the case of model samples of a total organic carbon content of < 1 g/l (1 g/1000g) proved to be less because of the detection limit of the constituents

Composition of selected samples containing bauxite organics (Table 12)

- The amount of any compound is highly charcteristic to the bauxite it is orginating from.
- For example Korba bauxite which has been analyzed 10 years earlier provided particularly high humic acid and oxalic acid contents.
- The ratios of the constituents identified in acidic digests compared to those dissolved in Bayer cycles varied considerably due to the different nature of bauxite organics and Bayer conditions applied .

Table 11

Components of 'cycle organics' determined as n-butylesters

Acids, expressed in % of the total Org. C	Plant		Halimba bx		Hal.bx & rye flour		Rye flour aluminate liquor	Koyna bx liquor
	liquor	hydr.	liquor	salt	liquor	salt		
Total org. C g/l (g/100 g)	6.66	0.207	0.399	0.0559	0.665	0.0923	4.81	0.435
Humic *1	3.6	2.0	1.2	3.1	1.0	1.6	-	14.4
Amino *2	3.3	n.m.	2.5	n.m	18.5	16	13.5	4.9
Formic	12.5	6.0	4.8	19.5	5.4	18.3	6.5	4.3
Acetic	36.0	23.9	15.8	5.6	11.3	5.0	20.0	8.9
Propionic	1.9	0.9	1.5	0.6	1.1	0.3	1.6	0.6
i-Butyric	0.5	0.5	0.1	0.1	0.1	0.1	0.2	0.1
n-Butyric	0.6	0.3	0.5	0.3	0.3	0.1	0.1	0.3
n-valeric	0.1	0.3	-	0.1	0.1	0.1	-	0.1
Oxalic	2.1	36.8	9.6	13.4	9.3	17.8	6.4	22.0
Benzoic	0.9	-	0.6	-	3.2	2.8	-	-
Succinic	5.2	8.0	2.0	0.8	2.1	1.8	15.3	0.1
Glutaric	1.2	3.8					-	-
Adipic	0.7	-	-	-	-	-	-	-
Pimelic	0.4	-	-	-	-	-	-	-
O-phthalic	1.1	1.0	15.6	10.3	14.8	10.4	-	2.8
Hemimellitic	-	0.5	0.1	-	-	-	-	0.1
Trimellitic	28.0	1.4	1.5	0.7	1.0	1.2	-	0.3
Trimesic	3.5	3.1	0.5	0.2	0.2	0.3	-	1.3
Pyromellitic	0.6	1.4	0.4	0.4	0.2	0.6	-	1.3
not identified	7.2	-	-	-	-	-	12.0	-
Measured in total	103.5	97.0	67.1	55.8	69.5	77.3	98.5 3*	62.6

* 1. Measured by their total organic carbon content
* 2. Measured as ammonia formed by the hypochlorite oxydation
* 3. Including 11.0 % lactic and 10 % glycolic acids respectively.

Table 12
Components of 'bauxite organics' determined as n-butylesters

Acids, expressed in % of the total Org. C			Bauxites				
	Halim-ba	Koyna	Weipa	Ghana-kibi	Ghana-Nyinahin	Jama-ica	Korba
Total Org. C g/100 g x 10^2	7.70	16.1	18.5	18.6	15.5	20.0	9.8
Humic 1*	3.2	8.1	10.8	7.0	7.4	7.5	9.8
Formic 2*	5.1	3.7	5.6	6.3	4.0	5.9	9.4
Acetic	17.4	8.2	5.0	13.4	9.6	5.8	15.2
Propionic	0.4	0.1	0.1	0.08	0.08	0.03	0.2
i- & n-Butyric	0.05	< 0.02	<0.02	< 0.02	< 0.02	< 0.02	0.05
i- & n-Valeric	0.08	< 0.02	<0.02	<0.002	<0.02	< 0.02	0.1
Oxalic	1.2	6.7	12.8	8.6	< 0.05	2.1	19.1
Succinic	< 0.02	0.4	1.0	< 0.02	< 0.02	2.0	0.9
O-Phthalic	3.8	1.6	0.8	0.2	0.1	0.7	0.2
Lauric	< 0.02	< 0.02	< 0.02	0.2	0.2	0.09	0.2
Miristic	0.2	0.1	0.3	0.2	0.4	0.2	0.5
Benzene tricar	0.9	0.5	0.5	0.2	0.8	0.2	1.0
Palmitic	1.4	0.7	0.7	0.4	1.3	0.5	1.9
Benzene tetrac	1.0	0.4	1.0	0.5	0.9	0.3	2.4
Stearic & Pyro	0.5	0.4	0.5	0.3	0.5	0.2	0.8
Indentified in total	35.2	30.9	39.1	37.4	25.3	24.9	61.8
Dissolved in 1 Bayer cycle	20	61	75	no data	available		75.0

REFERENCES

1. Maros . L., Schulek, I., Molnar-Perl, I., and Pinter-Szakacs. M., Anal.Chim. Acta, 25,1961,390
2. Maros, L., Pinter-Szakacs, M., and Schulek, E. , Anal. Chim. Acta., 27,1962,169
3. Molnar-Perl , I., Pinter- Szakacs,. M., Chromatographia,17, 1983, 328
4. Molnar-Perl ,I., Pinter- Szakacs,.M., Chromatographia,17, 1983, 497
5. Molnar-Perl ,I., Pinter- Szakacs,.M., Anal. Letters, 17A 11, 1984, 1325
6. Molnar-Perl, I., Kiasfaludi,A., Pinter- Szakacs, M., J.Chem. Eng. Data, 29, 1984, 66
7. Molnar- Perl, I.,Fabian - Vonsik, Pinter-Szakacs,M., Chromatographia, 18, 1984, 637
8. Molnar-Perl, I., Fabian- Vonsik, Pinter- Szakacs, M., Chromatographia, 18, 1984, 673
9. Molnar- Perl, I., and Pinter-Szakacs,M., Anal. Chim. Acta, 18, 1985, 353
10. Molnar-Perl, I., and Fabian- Vonsik, M., Chromatographia, 20, 1985, 421
11. Molnar-Perl, I., Fabian- Vonsik,V.,and Pinter- Szakacs,M., Chromatographia, 20, 1985, 605
12. Molnar- Perl, I., Pinter - Szakacs, M., J. Chromatogr., 365, 1986, 171
13. Molnar-Perl, I., Morvai, M., Chromatographia, 22, 1986, 329
14. Molnar-Perl, I., Morvai, M., Chromatographia, 23, 1987, 265
15. Molnar-Perl, I., Morvai, M., Chromatographia, 25, 1987, 37
16. Molnar-Perl, I., Morvai, M., Chromatographia, 23, 1987, 760
17. Morvai, M., Molnar-Perl, I., Chromatographia, 23, 1987,925
18. Molnar-Perl, I., Pinter - Szakacs,. M,. J. Chromatogr., 93, 1987, 434
19. Moravi., M., Molnar-Perl, I., Pinter - Szakacs,. M,. J. Chromatogr. 446, 1988, 237
20. Mariassy,. M., Borsiczky, V., Somogyi, I., Kohaszati, Lapok, 2, 1954, 73
21. Bogardi, E., Lectures given on Postgraduate course for engineers

22. Gedeon, T., Kohaszati Lapok 5, 1955, 229
23. Solymar , K., Feher, I., Magyarossy Zambo, J., Femipari Kutato Intezet Kozlememyei V. 1961, 29
24. Matyasi, J., Orban- Kelemen, M., Kohaszati Lapok 7, 1962, 310
25. Matyasi, J., Orban- Kelemen, M., Kohaszati Lapok 8, 1962, 343
26. Mathes, F., Bach, H. Chem. Techn. 14, 1962, 610
27. Sato, C., Kazama, S., TMS paper Selection : Paper No. A 71-11
28. Laszlo, E., Lux, A. Hollo, J., Die Starke 17, 1966, 188
29. Matyasi, J., Doctoral thesis 1963
30. Hollo, J., Laszlo, E., Szejtli, J., Die Starke 17, 1965, 36
31. Lanyi, B., Travaux du Comite International pour l'etude des Bauxites, des Oxydes et des Hydroxydes d' Aluminium 7, 1971, 59
32. Volf, F. F. Onti NKTP 86 - 114, 1935
33. Schepers, B., Erzmetall 29, 1976, 61
34. Hollo, J., Szejtli, J., Laszlo, E., Gartner, G.S. Toth, Zs., Huszar, J., Lux, A., Die Starke 16, 1964, 118
35. Hollo, J., Szejtli, J., Lux, A., Die Starke 16, 1964, 167
36. Lux, A., Laszlo, E., Huszar, J. Gartner, G.S., Hollo. J., Die Starke 19, 1967, 129
37. Paulik, I., Paulik,F.,: Thermal Analysis , Vol. 1 Proceedings Third I.C.T.A. ; Davos , 489, 1971
38. Molnar- Perl, I., Pinter-Szakacs, M., Maros, L., International Syposium on Microchemical Techniques 1977 Davos, Abst. p 83
39. Hungarian Patent Application : 10.11.1978.
40. Maros, L., Zsindely, S., Magy Kem. Folyoirat 68, 1962, 357
41. Shehyn, H., Anal. Chem.. 27, 1955, 61
42. Lever, G., Aime 107. Ann. Met. 1978 Denver, Light Metals Vol. II. p 71

DESCRIPTION OF THE METHODS HANDED OVER

INTRODUCTION

An overwhelming majority of alumina is produced all over the world by the Bayer process, a still living and unsolved problem of which is that of the organic substances, so-called "organics".

Organic substances enter the Bayer-cycle from two sources:

a) from bauxite to be processed,
b) from flocculants, applied for promoting the settling of red mud.

One part of the organic substances leaves the circuit finally or temporarily along with the red mud, alumina hydrate and soda salt. The other part of the organics accumulates gradually in the liquor phase of the circuit to equilibrium concentration and has undesirable effects on nearly all steps of the alumina production process.

It is known that organics are present in the liquor phase of the circuit as a mixture of a great number of organic compounds of different molecular weights, and their effects can be very diverse in various process steps. There is little knowledge available for the identification of the individual organic compounds present in the Bayer process circuit and for the mechanisms through which they exert their harmful influence. This fact can be explained by the complexity of the task.

To solve this problem the exact knowledge of the life and of the qualitative and quantitative changes of the individual organic compounds is indispensable. Such a complex and exact analytical method is required for this purpose which makes possible the reliable qualitative and quantitative determination of organic substances present in amounts between 10^{-5} and 1 per cent in different stages of oxidation in various materials of the alumina production cycle.

The complex analytical method elaborated by ALUTERV-FKI and ELTE makes possible the qualitative and quantitative determination of about 30 different organic compounds which represent 75 to 80 per cent of the total organics.

The above-mentioned analytical method can be split into two methods closely connected with each other:

a) Determination of the total organic content.
b) Selective qualitative and quantitative analysis of the individual organic components or groups.

Organics have always to be expressed in terms of carbon ("C_{org}") so that data of individual compounds can be easily handled and compared.

1. DETERMINATION OF TOTAL ORGANIC CARBON CONTENT IN MATERIALS OF THE BAYER ALUMINA PRODUCTION PROCESS

THE BASIC PRINCIPLE OF THE METHOD

Total organic carbon content, after elimination of the carbonate content of the samples to be investigated (bauxite, red mud, aluminate liquors, alumina hydrate, soda salt, etc.), has to be oxidized quantitatively to carbon dioxide. This oxidation takes place in an acidic medium with potassium peroxydisulphate ($K_2S_2O_8$) in the presence of a catalyst consisting of silver ions. The carbon dioxide set free during oxidation has to be distilled into a barium hydroxide measuring solution. The quantity of absorbed carbon dioxide is determined by titration of the excess of barium hydroxide with hydrochloric acid.

REAGENTS

Barium hydroxide solution 0.01N, containing 50 g/l barium chloride ($BaCl_2 \cdot 2H_2O$)

Preparation: 3.2 g barium hydroxide ($Ba/OH/_2 \cdot 8H_2O$, analytical grade) is dissolved in 200 ml distilled water and 100 g barium chloride ($BaCl_2 \cdot 2H_2O$, a.g.) is dissolved in 100 ml boiling distilled water. The two hot solutions are mixed and let stand over for 24 hours, then the volume is filled up to 2,000 ml with distilled water and filtered into the storing flask of an automatic burette. Previously n-pentane is poured into the storing flask up to cca. 10 mm height.

The burette (of 15-20 ml volume) is placed on the storing flask and closed by a glass tube filled with soda asbestos.

Hydrochloric acid solution 0.01N

It has to be prepared from a.g. hydrochloric acid by first diluting it to 0.1N, standardizing the latter using potassium hydrogen carbonate ($KHCO_3$) in the presence of methyl red indicator and subsequently diluting it to an exactly tenfold volume with distilled water.

Potassium hydrogen carbonate (a.g.)

30 weight per cent phosphoric acid solution free from organic substance

Preparation: 1 litre concentrated a.g. quality phosphoric acid (H_3PO_4) is heated up to boiling point, then some 0.5 g potassium peroxydisulphate ($K_2S_2O_8$) is added 3 times in small doses into the hot solution. The solution has to be kept in moderate boiling for another 1 to 1.5 hour. After cooling the volume of the solution has to be filled up with distilled water free from carbon dioxide and organics to 1,000 ml. This phosphoric acid will be diluted at a 3:1 (water to acid) ratio with distilled water free from carbonate and organics according to requirements.

Storing: In a glass stoppered flask. The glass stopper has to be covered by a bell-jar to protect it from dust.

Saturated potassium peroxydisulphate solution

Preparation: For the preparation of the solution a.g. $K_2S_2O_8$ purified by recrystallization and distilled water free from carbonate and organics have to be used. The saturated solution has to be prepared freshly every day.

At recrystallization some 250 g $K_2S_2O_8$ is dissolved in about 600 ml hot (60 to 80 °C) distilled water and the hot solution is filtered through a G-3 glass filter. (The glass filter has to be washed previously with a mixture of 50 ml 96 per cent sulphuric acid and 25 ml 30 wt. per cent H_2O_2, then rinsed with distilled water until pH drops to about 3.

$K_2S_2O_8$ crystals precipitated from the filtered and cooled solution are similarly filtered through a glass filter.

Storing: The purified wet crystals are stored in a glass stoppered flask. The glass stopper is protected by a bell-jar from dust.

Silver sulphate

Preparation: 1:4 sulphuric acid is added to saturated silver nitrate solution until precipitation does not occur anymore.

Storing: The decanted silver sulphate is stored in a wet form in a glass stoppered flask.

Distilled water free from carbonate and organics

Preparation: Distilled water has to be redistilled in a glass apparatus in the presence of silver sulphate (0.1 g/l), potassium peroxydisulphate (0.5 g/l) and holystone if a 20 ml sample of the distilled water - boiled for half an hour - consumes more than 0.20 ml 0.01N alkali equivalent to carbon dioxide. For the elimination of carbonate the distilled water free from organics has to be boiled for another half an hour in the presence of holystone. Carbonate elimination has to be repeated on each day of measurement.

Storing: in a flask covered by a glass beaker.

Thymol blue and methyl red indicator solutions

Preparation: Some 0.3 g thymol blue and the same amount of methyl red indicators are dissolved in 100 ml 96 per cent ethyl alcohol (ethanol a.g.) each.

n-pentane

Holystone

Grain size: 2 to 3 mm
The holystone has to be freed from organics by ignition at 500 °C for half an hour.

Storing: In a glass stoppered flask covered with a protecting bell-jar.

Copper wire (a.g.)

As used for microcombustion according to the Pregl combustion method.

N_2 gas. High purity (99,99 per cent).

H_2 gas.

EQUIPMENT AND APPARATUS

Apparatus for the elimination of carbon dioxide from aluminate liquor and soda salt samples:

See Fig. 1.

Parts:

(1) 100 ml glass stoppered spherical flask.

(2) Gas inlet pipe made from glass fitted into a glass stopper.

(3) N_2 gas cylinder with reducer (15 to 40 dm^3).

Apparatus for the elimination of carbon dioxide from bauxite, red mud and alumina hydrate samples:

See Fig. 2.

Parts:

(1) 100 ml glass stoppered spherical flask.

(2) Glass condenser.

(3) Hot plate. Output: 200 to 500 W.

Apparatus for determination of the total organic carbon content in bauxite, red mud, alumina hydrate, aluminate liquor and soda salt samples previously freed from carbon dioxide:

See Fig. 3.

Parts:

(1) 100 ml glass stoppered spherical flask.
(2) H_2 gas inlet pipe.
(2a) H_2 gas cylinder with reducer (15 to 40 dm^3).
(3) Distributing pipe.
(4) Quartz pipe filled with copper wire.
(5) Feed funnel.
(6) Glass stopper.
(7) Cooler with water connections (7a, 7b, 7c, 7d).
(8) 100 ml glass stoppered Erlenmeyer flask for carbon dioxide absorption.
(8a) Glass tube filled with soda asbestos inserted into a rubber plug with two borings.
(9) Heating coil, wound round quartz pipe (4). Power regulated by a toroid transformer.
(10) Low inertia electric heater. Power regulated by a toroid transformer.
(11 to 14) Ground joints of parts 1,3,4,5 and 7.

1.1 PREPARATION OF THE SAMPLES: CARBON DIOXIDE ELIMINATION

The task of sample preparation is the elimination of the carbon dioxide content of materials to be examined.

During elimination of carbon dioxide a very important condition is to avoid any loss of organic substance. The method and apparatus used for carbon dioxide elimination depend on the samples to be investigated.

1.1.1 Preparation of aluminate liquor and soda salt samples

Preparation of these materials is carried out in the apparatus shown in Fig. 1.

A portion of aluminate liquor or soda salt stock solution, containing 300 to 600 µg of organics expressed in organic carbon, is measured into reaction flask 1.

After adding 20 ml 30 weight per cent (i.e. 3:1) phosphoric acid and inserting gas inlet pipe 2, high purity N_2 gas is passed through the solution for 30 minutes at room temperature with such an intensity that the bubbles can just not be counted.

After 30 minutes the preparation (carbon dioxide elimination) of the sample can be considered as accomplished, therefore, N_2 gas introduction is stopped. Total organic content is determined according to para 1.2.3.1.

1.1.2 Preparation of bauxite, red mud and alumina hydrate samples

For preparation of the samples the apparatus shown in Fig. 2 is used. A sample of air-dry alumina hydrate or bauxite or red mud having a grain size less than 0.05 mm is weighed on an analytical scale into reaction flask 1 in such an amount that the quantity of organics be between 300 and 600 µg expressed in organic carbon. Pulverized samples have to be introduced into the flask through a long stem funnel.

After adding 20 ml 30 weight per cent phosphoric acid solution and fitting condenser 2 the content of the reaction flask is kept in uniform smooth boiling for about 1.5 to 2.0 hours.

After boiling is finished the condenser should be washed back into the flask by maximum 5 ml distilled water free from carbon dioxide and organics.

Total organic content is determined from the sample prepared this way according to para 1.2.3.2.

1.2 DESCRIPTION OF THE MEASUREMENT OF TOTAL ORGANIC CARBON CONTENT

1.2.1 Preparation of the apparatus for determining total organic carbon content

H_2 gas inlet pipe 2 is fitted to ground joint 11 of the apparatus (Fig. 3) and ground joint 12 is closed by stopper 6. The ground joints are fixed by springs and the end of the cooler is immerged to a depth of 1 to 1.5 cm into water poured into flask 8. Then high purity H_2 gas is led through the device from H_2 gas cylinder 2a with an intensity of 2 to 3 bubbles/sec for 1 minute in order to drive out the air. After that heating coil 9 is made glow by a toroid transformer and the copper wire filling is reduced to pure metallic copper. The end of the reduction (1 to 2 minutes) is indicated by the red colour of the filling material.

After switching off heater 9 H_2 gas introduction is continued until the copper filling cools down, then the H_2 gas is shut off, too, and flask 8 is disconnected from beneath the stem of the cooler. For finishing the preparation glass stopper 6 and gas inlet pipe 2 are removed, feed funnel 5 is placed back into ground joint 12, and finally the funnel is filled up with distilled water free from carbon dioxide and organics.

Note: The preparation (reduction) of the copper wire filling should be carried out before each measurement.

1.2.2 Determination of the operational blank value

The accuracy of measuring requires a reliable reproducibility of the operational blank value. When determining the blank value all procedures of the carbon dioxide elimination and organics determination should be carried out with the prescribed quantities of chemicals, observing the required time of each procedure, but without adding the samples themselves.

Note: The operational blank value is to be determined every day before beginning the investigations or when using a chemical for the first time.

1.2.2.1 Determination of the blank value when analysing aluminate liquors or soda salt

10 ml distilled water free from carbon dioxide and organics and 20 ml 30 per cent phosphoric acid are put into reaction flask 1 of the apparatus shown in Fig. 1. N_2 gas is conducted through the solution for 30 minutes with such a flow intensity that the bubbles can just not be counted.

Parallel to this procedure 20 ml distilled water free from carbon dioxide and organics and 3 ml saturated potassium peroxydisulphate solution are put into flask 1 of the apparatus shown in Fig. 3, and some 0.1 g of holystone and some 0.1 to 0.2 g of silver sulphate is added.

Flask 1 is fitted to ground joint 11 and heating 10 is switched on.

The content of flask 1 is brought to boil and kept uniformly boiling with the help of heater 10. When the vapours leave cooler 7, heater 9 is switched on.

During the procedure there is no cooling water in the mantle of cooler 7, and flask 8 is not under it.

The apparatus becomes free from air within 2 minutes, then flask 8 is fitted to the end of cooler 7. Previously about 5 ml n-pentane should be poured into the flask, then exactly 15 ml 0.01N $Ba(OH)_2$ solution has to be let in from a burette.

Opening the water tap and stopcock 7d, the vapours condense and the $Ba(OH)_2$ solution is sucked up to about one third of the height of the cooler.

Thereafter the blank solution prepared in the apparatus shown in Fig. 1 is poured into feed funnel 5 of Fig. 3 (stopcock is closed) and is allowed to flow down in small portions into flask 1. While feeding the blank solution the content of flask 1 should be kept in constant boiling.

The blank solution has to be allowed to flow down to the stopcock of the feed funnel, then flask 1 of Fig. 1 has to be washed out 3 times with 2 ml distilled water each time. Wash water has to be added into flask 1 of Fig. 3 through funnel 5 as well.

After adding the blank solution and wash water, 20 ml saturated potassium peroxydisulphate solution is poured into funnel 5, which has to be added into flask 1 in frequent, small doses during the 30 minute time period of oxidation and distillation.

The level of the $Ba(OH)_2$ solution sucked up into cooler 7 can be raised or lowered by changing the outlet height of the cooling water (operating stopcocks 7a, 7c and 7d).

Subsequent to the oxidation and distillation the cooling water is let out from the cooling mantle of cooler 7 through stopcock 7d. The solution flows from the cooler into flask 8 under the pressure in the apparatus.

After emptying cooler 7, flask 8 is lowered so that the end of the cooler does not reach the liquid. By simultaneously opening the water tap and stopcock 7a (7c and 7d are closed) the cooler is completely filled up with water.

By further boiling the content of flask 1 for one minute the apparatus is washed out with vapour and condensate, subsequently flask 8 is disconnected from the end of the cooler and closed by a ground glass stopper.

Concluding steps of the procedure are the following:

- cooling water is let out from cooler 7 by opening stopcock 7d and turning off the water tap,
- the stopcock of feed funnel 5 is opened,
- heaters 9 and 10 are switched off.

1.2.2.2 Determination of the blank value in case of bauxite, red mud and alumina hydrate analyses

20 ml 30 weight per cent phosphoric acid solution is poured into reaction flask 1 of the apparatus shown in Fig. 1. After inserting condenser 2 the content of flask 1 is kept in mild boiling for 45 minutes, then heating 3 is switched off, the condenser is washed with 2 to 3 ml distilled water into flask 1 and its content is allowed to cool to room temperature.

Simultaneously with the above procedure the apparatus shown in Fig. 3 is prepared (see para 1.2.1 and 1.2.2.1 up to feeding the blank solution). The blank solution prepared in the apparatus shown in Fig. 2 is poured into feed funnel 5. Subsequently the procedure is carried out as described in para 1.2.2.1 with the difference that oxidation and distillation are carried on for 45 minutes and some 30 ml saturated potassium peroxydisulphate solution is added in frequent, small doses during this time period.

Note: The operational blank value should be the same when carrying out the elimination of carbon dioxide according to the procedures described in either para 1.1.1 or para 1.1.2 or at least the difference between them should not exceed ±0.1 ml supposed that the reagents used are pure and the procedures are adhered to. If so, the elimination of carbon dioxide can be omitted.

1.2.2.3 Measurement and calculation of the operational blank value

Some 5 ml n-pentane is poured into a 100 ml glass stoppered Erlenmeyer flask. 15 ml 0.01N $Ba(OH)_2$ solution is let from a burette into the flask and 5 to 6 drops of thymol blue indicator solution is added.

The $Ba(OH)_2$ solution has to be titrated with 0.01N hydrochloric acid solution. During titration the flask should be closed and shaken frequently. Near to the titration endpoint the HCl solution should be added dropwise and after each drop the flask has to be shaken thoroughly. The change of the indicator's colour from blue to green shows the endpoint of the titration.

Consumption: V_1 ml 0.01N HCl

The solution collected in flask 8 according to para 1.2.2.1 or 1.2.2.2 has to be titrated with 0.01N hydrochloric acid standard solution in the presence of thymol blue indicator with the same titrating prescriptions.

Consumption: V_2 ml 0.01N HCl

The following formula is used for the calculation of the operational blank value:

$$B_v = (V_1 - V_2) \cdot f \text{ ml 0.01N HCl solution,}$$

where:

B_v is the operational blank value expressed in mls of 0.01N HCl solution,

V_1 is the volume of 0.01N HCl solution consumed for titrating 15.00 ml 0.01N $Ba(OH)_2$ solution (ml),

V_2 is the volume of 0.01N HCl solution consumed for titrating the 15.00 ml 0.01N $Ba(OH)_2$ solution collected when determining the operational blank value (ml),

f is the factor of the 0.01N HCl solution.

The blank value shall not be higher than 0.8 ml 0.01N HCl solution ($B_v \leq 0.8$) and if measured repeatedly, the deviation shall not be higher than ±0.1 ml 0.01N HCl solution.

An example for calculating the operational blank value:

14.35 ml 0.01N HCl (V_1) is consumed for the neutralization of 15.00 ml 0.01N $Ba(OH)_2$ solution. After carrying out the described procedures 13.85 ml 0.01N HCl (V_2) is consumed for the neutralization of the 15.00 ml 0.01N $Ba(OH)_2$ solution. The operational blank value calculated from the above data is:

$$B_v = (V_1 - V_2) \,.\, f = (14.35 - 13.85) \,.\, 1.015 = 0.51 \text{ ml}$$

0.01N HCl solution.

1.2.3 Determination of the total organic carbon content

1.2.3.1 Determination of the total organic carbon content of aluminate liquor and soda salt samples

For the sake of exact measurement the total organic carbon content should be between 300 and 600 μg in the aluminate liquor samples. The usual total organic carbon content of aluminate liquors is some 8 to 12 g/l.

Consequently the amount of liquor used for one determination is:

$$\frac{450}{\frac{10 \,.\, 10^6}{10^3}} = \frac{450 \,.\, 10^3}{10^7} = 0.045 \text{ ml}$$

original aluminate liquor.

(450 µg is the mean value of 600 and 300 µg, 10 g is the mean value of the estimated 8 to 12 g organic carbon content.)

This value is well approached by taking out 5 ml from the hundredfold diluted stock solution (10 ml original liquor diluted to 100 ml, then out of this solution 10 ml diluted repeatedly to 100 ml).

$$\frac{10}{100} \cdot \frac{10}{100} \cdot 5 = 0.050 \text{ ml}$$

When analysing soda salt a stock solution is prepared so that 5 to 10 ml of it contains 300 to 600 µg organic carbon.

If e.g. the expected total organic carbon content is between 2 and 3 per cent,

$$\frac{450}{\frac{2.5 \cdot 10^6}{100}} = 0.018 \text{ g}$$

is weighed in from the soda salt for every 5 ml stock solution, therefore, 250 ml stock solution is prepared from $\frac{250}{5} \cdot 0.018 = 0.900$ g soda salt.

Further on an aliquot part of the aluminate liquor or soda salt stock solution is used for determining the organic carbon content (C_{org}).

The aliquot part (5 ml) taken out is freed from carbon dioxide according to para 1.1.1. The solution is poured into feed funnel 5 of the apparatus shown in Fig. 3 prepared for measuring according to para 1.2.1 and 1.2.2.1. The flask used for the elimination of carbon dioxide should be washed out three times with 2 ml distilled water free from carbon dioxide and organics at a time. The wash water is also added into flask 1 through funnel 3. Subsequently oxidation and distillation is carried out according to para 1.2.2.1 and titration according to para 1.2.2.3. The quantity of organic carbon can be calculated by the following formula:

$$Q_1 = /V_1 - (V_1 - V_2) - V_3/ \,.\, f \,.\, 0.06 \quad (\text{mg } C_{org}) \qquad (1)$$

where:

Q_1 is the organic carbon content of the sample (mg),

V_1 is the volume of 0.01N HCl solution consumed for titrating 15.00 ml 0.01N $Ba(OH)_2$ solution (ml),

V_2 is the volume of 0.01N HCl solution consumed for titrating 15.00 ml 0.01N $Ba(OH)_2$ solution collected when determining the operational blank value (ml),

V_3 is the volume of 0.01N HCl solution consumed for titrating the 15.00 ml 0.01N $Ba(OH)_2$ solution collected when analysing the sample (ml),

f is the factor of the 0.01N HCl solution,

0.06 is one hundredth of the equivalent mass of carbon.

The organic carbon concentration of aluminate liquors can be calculated by formula (2):

$$C_{org} = \frac{Q_1}{V} \quad g/l \qquad (2)$$

where:

Q_1 is the organic carbon content of the liquor sample (mg)

V is the aluminate liquor content of the aliquot part used for the determination of the organic carbon concentration (ml).

E.g. subsequent to the oxidation of 5 ml of the hundredfold diluted aluminate liquor solution 5.20 ml of 0.01N HCl (V_3) was consumed when titrating the 15.00 ml 0.01N $Ba(OH)_2$ solution. The 15.00 ml 0.01N $Ba(OH)_2$ solution originally consumed 14.35 ml 0.01N HCl (V_1). A similar volume of 0.01N $Ba(OH)_2$ solution consumed 13.85 ml 0.01N HCl (V_2) when determining the operational blank value. The factor of the 0.01N HCl solution was 1.015.

The organic carbon concentration of the aluminate liquor was:

$$C_{org} = \frac{Q_1}{V} = \frac{/14.35 - (14.35 - 13.85) - 5.20/ \;.\; 1.015 \;.\; 0.06}{\frac{10}{100} \;.\; \frac{10}{100} \;.\; 5} = 10.5 \text{ g/l}$$

The organic carbon concentration of soda salt can be calculated by formula (3):

$$C_{org} = \frac{Q_1}{W} \;.\; 100 \text{ per cent} \qquad (3)$$

where:

Q_1 is the organic carbon content of the soda salt sample (mg),

W is the soda salt content of the aliquot part used for the determination of the organic carbon content (mg).

E.g. 900 mg soda salt was weighed in and diluted to 250 ml volume. 5 ml of this stock solution was taken out for analysis. After oxidation 6.30 ml 0.01N HCl solution (V_3) was consumed when titrating the 15.00 ml 0.01N $Ba(OH)_2$ solution. The 15.00 ml 0.01N $Ba(OH)_2$ solution originally consumed 14.35 ml 0.01N HCl (V_1). A similar volume of 0.01N $Ba(OH)_2$ solution consumed 13.85 ml 0.01N HCl (V_2) when determining the operational blank value. The factor of the 0.01N HCl solution was 1.015.

The organic carbon concentration of the soda salt was:

$$C_{org} = \frac{Q_1}{W} \cdot 100 = \frac{/14.35 - (14.35 - 13.85) - 6.30/ \cdot 0.06 \cdot 1.015 \cdot 100}{\frac{900}{250} \cdot 5} =$$

$$= 2.55 \text{ per cent}$$

Accuracy of the organic carbon measurement for aluminate liquors and soda salt is ±3 rel. per cent.

1.2.3.2 Determination of the total organic carbon content of bauxite, red mud and alumina hydrate samples

The samples should be selected so that they contain 300 to [illegible]00 ug organic carbon.

The carbon dioxide content of the samples is eliminated according to para 1.1.2. The operational blank value is determined according to para 1.2.2.2.

The slurry sample free from carbon dioxide is poured into funnel 5 of the apparatus shown in Fig. 3 prepared for measuring according to para 1.2.1 and 1.2.2.1. The flask used for the elimination of carbon dioxide should be washed out three times with about 2 ml distilled water free from carbon dioxide and organics at a time. The wash water is also added into flask 1 through funnel 5.

Subsequently oxidation and distillation is carried out according to para 1.2.2.2 and titration according to para 1.2.2.3. The quantity of organic carbon can be calculated by the following formula:

$$Q_1 = /V_1 - (V_1 - V_2) - V_3/ \; . \; f \; . \; 0.06 \quad (\text{mg } C_{org}) \qquad (2$$

(For abbreviations used see para 1.2.3.1.)

The organic carbon content of the samples can be calculated by formula (3):

$$C_{org} = \frac{Q_1}{W} \; . \; 100 \text{ per cent} \qquad (3$$

E.g. 231.2 mg bauxite sample (W) was weighed in. After oxidation 5.00 ml 0.01N HCl solution (V_3) was consumed when titrating the 15.00 ml 0.01N $Ba(OH)_2$ solution. The 15.00 ml 0.01N $Ba(OH)_2$ solution originally consumed 14.35 ml 0.01N HCl solution (V_1). A similar volume of 0.01N $Ba(OH)_2$ solution consumed 13.90 ml 0.01N HCl solution (V_2) when determining the operational blank value. The factor of the 0.01N HCl solution was 1.015.

The organic carbon content of the bauxite sample was:

$$C_{org} = \frac{Q_1}{W} \; . \; 100 = \frac{/14.35-(14.35-13.90)-5.00/ \; . \; 0.06 \; . \; 1.015 \; . \; 100}{231.2} =$$

$$= 0.23 \text{ per cent}$$

Accuracy of the organic carbon measurement for bauxite, red mud and alumina hydrate is ±5 rel. per cent.

2. DETERMINATION OF HUMIC ACID CONTENT IN MATERIALS OF THE BAYER ALUMINA PRODUCTION PROCESS

PRINCIPLE OF THE METHOD

That part of the total organics content of the investigated samples (bauxite, red mud, aluminate liquors, alumina hydrate, soda salt) is understood by humic acids which is insoluble in mineral acids, however, readily dissolves in caustic liquors giving a brown colour to them. Their quantity can be determined

- spectrophotometrically (on the basis of a real, existin relationship between organic carbon content and extinction of their alkaline solutions), or
- on the basis of carbon dioxide formed during their oxid. tion with potassium peroxydisulphate.

REAGENTS

Sulphuric acid, prepared by mixing 22.5 ml 98 weight per cent sulphuric acid and 77.5 ml distilled water free from carbon dioxide and organic matter.

Sodium hydroxide solution 1M.

EQUIPMENT AND APPARATUS

Spectrophotometer with 1 cm cuvettes.

Vacuum rotary evaporator with 50 and 1,000 ml glass stoppered flasks.

Glass microfibre paper, GF/81, Whatman product.

50 and 100 ml beakers.

Dia 3.5 to 4 and 8 to 10 cm funnels.

5 to 250 ml volumetric flasks.

Dia 8 to 10 cm G-3 glass filter.
Filtering bell connected to water jet vacuum.

2.1 PREPARATION OF THE SAMPLES: PRECIPITATION AND PREPARATION OF THE STOCK SOLUTION OF HUMIC ACIDS

2.1.1 Preparation of concentrated aluminate liquors (containing some 140 to 260 g/l caustic Na_2O)

A 5 to 10 ml aliquot of aluminate liquor measured with analytical accuracy, containing at least 0.05 g organ carbon, is mixed with the double volume of sulphuric acid a beaker and the mixture is covered by a watchglass. Afte at least 3 hours from the dissolution of salts – which is promoted by stirring - the precipitated humic acids are filtered on a dia 3.5 to 5 cm funnel covered with glass microfibr paper. After quantitatively filtering the solution the humic acids on the filter paper are washed with some 50 ml distilled water to about pH = 3. The beaker used for the precipitation of humic acids is washed with each 5 ml port of the distilled water. A 5 to 100 ml 1M alkaline stock solution is prepared, depending on their quantity, from th humic acids on the filter with 1 to 2 ml portions of the 1 sodium hydroxide solution. The beaker used for the precip tation of the humic acids is washed with each portion of t sodium hydroxide solution, too.

Remarks:

- A small quantity of humic acid can be quantitatively dissolved even with 5 ml sodium hydroxide solution.
- Should the solution prepared be turbid, it has to be filtered again.

2.1.2 Preparation of weak caustic liquors (containing les than about 140 g/l caustic Na_2O)

A portion of the weak caustic liquor measured with analytical accuracy, containing at least 0.05 g organic carbon, is concentrated on a water bath or in a vacuum rot evaporator to about 200 g/l caustic Na_2O concentration. Th concentrated liquor is mixed with the double volume of sulphuric acid and the procedure is carried on further according to para 2.1.1.

2.1.3 Preparation of soda salt

0.5 to 10 g soda salt measured with analytical accuracy is homogenized with 10 ml distilled water, then mixed with 5 to 30 ml sulphuric acid. The procedure is carried on further according to para 2.1.1.

2.1.4 Preparation of alumina hydrate

50 g alumina hydrate measured with an accuracy of 0.01 g is placed in a G-3 glass filter fitted on a filtering bell and washed with 20 to 50 ml portions of 500 ml ho distilled water. The portions of wash water are let to pass the filter without using vacuum. After the dropping stops, the remaining solution is sucked off by vacuum. Th combined washing solution is dried by evaporating it in th 1,000 ml flask of the vacuum rotary evaporator. The salt remaining in the flask is washed with 25 ml distilled wate into a beaker and mixed with 10 ml sulphuric acid. The procedure is carried on further according to para 2.1.1.

2.1.5 Preparation of bauxite and red mud

The digest prepared from 5 g of bauxite or red mud measured with an accuracy of 0.001 g with 60 ml sulphuric acid according to para 3.2.1.3 is delivered after continuo liquid-liquid (c.l./l. further on) etheric extraction or without extraction quantitatively into a dia 8 to 10 cm funnel covered by glass microfibre paper. The digest is washed with distilled water and a 250 ml stock solution (which can be used for the determination of the acid solub. bauxite and red mud organics based on the measurement of total organic carbon content) is prepared by combining the washing solutions. The pH of the last portion dropping from the filter, containing the digest, should be at least 3 The digest remaining on the filter paper is washed with portions of hot sodium hydroxide solution until the solution passing the filter becomes colourless. By combining the alkaline solutions of humic acids a stock solution is prepared.

2.2 DESCRIPTION OF THE MEASUREMENT OF HUMIC ACID CONTENT

2.2.1 Approximate spectrophotometric determination of humic acid content

Extinction of the alkaline solution of humic acids is measured at 380 nm against a 1M sodium hydroxide solution. The aim of the spectrophotometric measurement is the approximate determination of humic acid content. According to experiences obtained up to now the spectrophotometric carbon equivalent relative to E = 0.100 of alkaline solutions of humic acids expressed in organic carbon is 7.4 μg/ml for humic acids originating from liquo and 5.0 μg/ml for those originating from bauxites.

2.2.2 Determination of humic acid content on the basis of measuring total organic carbon content of their alkaline solutions

A portion of the solution of humic acids estimated according to para 2.2.1 to contain 60 to 300 µg organic carbon and measured with analytical accuracy is mixed with 20 ml phosphoric acid prepared according to para 1 and is freed from carbonate by boiling it for 30 minutes in the apparatus shown in Fig. 2 according to para 1.1.2. The flask, containing the phosphoric acid solution of humic acids, is connected as a distilling flask to the apparatus serving for the determination of total organic carbon shown in Fig. 3. Care should be taken to free the apparatus (first of all its feed funnel) from persulphate by thoroughly washing it with distilled water. Oxidation of humic acids is carried on for 45 minutes according to para 1.2.3

3. QUALITATIVE AND QUANTITATIVE DETERMINATION OF CARBOXYLIC ACID CONTENT IN MATERIALS OF THE BAYER ALUMINA PRODUCTION PROCESS BY GASCHROMATOGRAPHY

THE BASIC PRINCIPLE OF THE METHODS

The overwhelming majority of carboxylic acids prese in materials of Bayer process alumina production can be transformed quantitatively into esters with alcohols in th presence of mineral acids in the inorganic matrix itself without any separation; and can be evaluated qualitatively and quantitatively as n-butyl ester from a single solution the basis of a single chromatogram.

The sterically hindered carboxylic groups of aromat carboxylic acids - positioned on adjacent carbon atoms of the aromatic core - can be esterified only with diazometha Such aromatic carboxylic acids are: mellitic acid (benzene hexacarboxylic acid), benzene pentacarboxylic acid and pre ic (1,2,3,4 benzene tetracarboxylic) and mellophanic (1,2,3,5 ben tetracarboxylic) acids among the tetracarboxylic acids.

3.1 QUICK DETERMINATION OF ALL CARBOXYLIC ACIDS AS BUTYL ESTERS ESTERIFIABLE WITH ALCOHOLS IN THE PRESENCE OF MINERAL ACIDS

REAGENTS

Sulphuric acid 98 per cent (a.g.) and 2M
NaOH solution 0.2M and 0.02M
n-Butyl alcohol (a.g.)
Anhydrous sodium sulphate (a.g.)
Chloroform (a.g.)

Synthetic aluminate liquor

Calibrating standard solution containing the following components weighed in with analytical accuracy:

		C, per cent
0.4 - 0.5 g	formic acid	26.07
1.0 - 1.2 g	acetic acid	39.96
0.06-0.07 g	propionic acid	48.65
0.03-0.04 g	i-butyric acid	54.48
0.03-0.04 g	n-butyric acid	54.48
0.05-0.06 g	i-valeric acid	58.75
0.02-0.03 g	n-valeric acid	58.75
0.4 - 0.6 g	crystallic sodium oxalate	19.03
0.05-0.06 g	benzoic acid	68.78
0.12-0.20 g	succinic acid	40.65
0.05-0.06 g	glutaric acid	45.42
0.03-0.04 g	adipic acid	49.27
0.01-0.02 g	pimelic acid	52.44
0.05-0.06 g	o-phthalic acid	57.79
0.01-0.02 g	hemimellitic acid (2 H_2O)	43.81
0.04-0.06 g	trimellitic acid	51.37
0.04-0.06 g	trimesic acid	51.37
0.04-0.06 g	pyromellitic acid (2 H_2O)	41.23
*0.04-0.06 g	prehnitic acid	47.26
*0.04-0.06 g	mellophanic acid	47.26
*0.04-0.06 g	benzene pentacarboxylic acid	44.31
*0.04-0.06 g	mellitic acid	42.12

* Only calibrating solutions prepared with diazomethane contain them.

CHROMOSORB W.A.W. D.M.C.S. (80 to 100 mesh) solid (Applied Sc. Lab.)

Dexsil 300 G.C. (Applied Sc. Lab.)

Glass wool (a.g.)

N_2 gas. High purity (99.99 per cent)

H_2 gas

Compressed air (in cylinder)

EQUIPMENT AND APPARATUS

Gaschromatograph

It has to be provided with an evaporator and a flame ionisation detector heatable up to 450 °C, a thermostat heating programable between 30 and 400 °C and an automatic cooling.

Integrator with a base line corrector.

pH-meter with a combined glass electrode.

Vacuum rotary evaporator with 50 to 1,000 ml glass stoppered flasks.

Water bath.

Drying oven.

10 µl syringe: S.G.E. Australian made.

Esterifying vessels

50 ml vessels with dia 35 mm ground necks, provided with condensers, into which glass stirrers (sticks with four branches, see Fig. 4) reach through the condensers; 5 ml sperical flasks with dia 14 mm ground necks, provided with condensers; ground glass stoppers for the esterifying vessels.

50 to 500 ml shaking funnels.

Tulip funnels for filtration of chloroformic solutions of esters (see Fig. 5).

5, 20 and 50 ml oval and spherical flasks with ground joi fitting to the vacuum rotary evaporator.

Measuring tubes

0.5 to 3 ml glass-stoppered test tubes calibrated for 0.5 ml (the 0.5 ml tuber for 0.1 ml) for storin stock solutions of butyl esters.

Inner dia 3 mm, 2 m long or inner dia 4 mm, 3 m long stainle steel columns.

3.1.1 PREPARATION OF THE SAMPLES: N-BUTYLESTERIFICATIONS

3.1.1.1 Butylesterification of carboxylic acid content of aluminate liquors

3.1.1.1.1 Direct process (for concentrated solutions)

1 ml aluminate liquor is pipetted (with analytical accuracy) into the esterifying vessel and mixed with 3 ml buta A glass stirrer is placed into the vessel and after wettin the ground joint of the condenser with one drop of concentrated sulphuric acid, the latter is fitted to the esterif ing vessel. Subsequently 2 ml concentrated sulphuric acid is added dropwise under stirring into the esterifying vessel through the condenser. The mixture is repeatedly homogenized with the help of the glass stirrer until sodiu sulphate precipitates (some 1 to 2 minutes), then esterification is continued for at least 40 minutes in a hot water bath. Subsequently the esterifying vessel is cooled to 15 to 20 °C by putting it into water and the condenser is

washed into the flask with 2 ml chloroform. After dismantling the vessel from the condenser its content is quantitatively washed into a 200 ml shaking funnel with a further 3 ml chloroform and 100 ml distilled water. (If it is necessary, the content of the vessel - closed with a glass stopper - has to be shaken with the mixture of chloroform and distilled water until the salts are completely dissolved.)

The content of the shaking funnel is shaken for one minute. After a complete separation of the phases the chloroformic phase is discharged into another shaking funnel, containing 100 ml distilled water and 1 ml 2M sulphuric acid. The extraction is repeated twice more wit 5 ml chloroform each time as described above. The 15 ml chloroformic solution of the esters is shaken again with another 100 ml of water for one minute, then the extraction is repeated twice again with 5 ml chloroform each ti The chloroformic solution of the esters extracted from the second 100 ml of water is collected for the third time in a shaking funnel, containing 100 ml distilled water, and is shaken for one minute. Then it is let down through a tulip funnel, containing cotton wool and sodium sulphate, into a 50 ml oval flask fitting to the ground joint of the vacuum rotary evaporator. The extraction is finished with a further 2 x 5 ml chloroform. The sodium sulphate-contai ing tulip funnel is washed with 1 to 2 ml chloroform.

The combined chloroformic solution of butyl esters i first concentrated to some 2 to 3 ml in the vacuum rotary evaporator using room temperature water for heating, then the solution is quantitatively transferred into a 5 ml ova flask and concentrated to 0.5 to 0.8 ml. Subsequently the solution is transferred into a calibrated tube and a 1 ml stock solution is prepared from it.

3.1.1.1.2 Process after previous neutralization and drying (for diluted solutions)

An aliquot of aluminate liquor, containing 0.025 to 0.05 g organic carbon and measured with analytical accuracy is pipetted into the esterifying vessel. If the caustic Na_2O concentration of the liquor is higher than 100 g/l, it is diluted with distilled water to 100 g/l caustic Na_2O concentration or less.

The solution is neutralized under water cooling by 2M sulphuric acid - with the help of a pH-meter or indicato paper - to pH 9 to 10, then it is dried in a vacuum rotary evaporator. In case of a large series of measurings, when a number of samples are prepared at the same time, drying is carried out in an oven set at 130 °C temperature. The dry residue is collected on the bottom of the vessel using a metallic spatula, then it is mixed with 0.5 ml water and 3 ml butanol. The condenser - after wetting its ground joint with one drop of concentrated sulphuric acid - is fitted to the esterifying vessel. 2 ml concentrated sulphuric acid is added dropwise under stirring through the co denser into the esterifying vessel which is subsequently placed into a hot water bath. After esterifying for at least 40 minutes the vessel is cooled to room temperature by placing it into water and the condenser is washed with 5 ml chloroform into the vessel. The content of the vessel - after dismantling it from the condenser - is quantitatively transferred into a shaking funnel with further 5 ml chloroform and 200 ml distilled water. If necessary, the ve sel is closed with a fitting glass stopper and its content is shaken with portions of the 200 ml distilled water until the salts are completely dissolved.

The content of the shaking funnel is shaken for one minute. After a complete separation of the phases the chloroformic phase is let down into a second shaking funne containing 200 ml distilled water and 2 ml 2N sulphuric acid. The extraction is repeated twice more with 10 ml chloroform each time as described above. The 30 ml chloroformic solution of esters is filtered through a tulip funn containing cotton wool and sodium sulphate, into a 50 ml oval flask. The extraction is finished with further 2x10 chloroform. The sodium sulphate in the funnel is washed with 1 to 2 ml chloroform.

After concentrating the combined chloroformic solution of butyl esters to 2 to 2.5 ml in a vacuum rotary evaporator using room temperature water for heating, it is quantitatively transferred into a calibrated tube and a 3 stock solution is prepared from it.

3.1.1.2 Butylesterification of carboxylic acid content of soda salt and alumina hydrate (direct process)

0.2 to 1.0 g salt is weighed with analytical accura or 5 to 10 g alumina hydrate, containing maximum 20 per ce moisture, with 0.001 g accuracy into the butylesterifying vessel. The organic carbon content of the salt or alumina hydrate should be at least 0.008 g. A glass stirrer is placed into the vessel and 0.5 ml water and 3 ml butanol are poured into it. Then the condenser is fitted on the esterifying vessel after wetting its ground joint with one drop of concentrated sulphuric acid. 2 ml concentrated sulphuric acid is added dropwise under stirring through the condenser into the esterifying vessel, which is subsequently placed into a hot water bath.

The procedure should be further carried out according to para 3.1.1.1.2 with the following differences:

- in case of alumina hydrate the first portion of the extract of the chloroformic extraction is transferred through a filter, containing 1 to 2 g sodium sulphate on cotton wool in order to retain the insoluble parts into the second shaking funnel, containing 200 ml wate and
- the combined solution of butyl esters filtered through sodium sulphate is concentrated to 1.5 to 1.6 ml and a 2.0 ml stock solution is prepared from it.

3.1.1.3 Butylesterification of carboxylic acid content o bauxite and red mud

3.1.1.3.1 Direct process: esterification combined with digestion

1.0 g bauxite or red mud weighed with 0.001 g accuracy is put into an esterifying vessel provided with a glass stirrer and it is stirred to a homogeneous slurry with 1.25 ml water. The condenser is fitted on the ester fying vessel after wetting its ground joint with one drop of concentrated sulphuric acid. 2 ml concentrated sulphuric acid is added dropwise under stirring into the latter through the condenser to avoid the possible heavy foaming. Digestion is continued without butanol by stirring the mixture several times for 10 to 15 minutes. Subsequently 3 ml butanol is introduced through the condense into the esterifying vessel and the content of the latter is stirred up. The insoluble part of the digest is floating in the solution in a loose form. Esterification combined with digestion is carried out for 2 hours in a water bath. Then the esterifying vessel is cooled to room temperature by placing it into water and the condenser is was ed with 5 ml chloroform into the vessel. After dismantling the vessel from the condenser the esterified digest of bau ite or red mud is quantitatively transferred with 100 ml distilled water into a shaking funnel.

The content of the shaking funnel is shaken for one minute. After separation of the phases but after at least 10 min waiting time the chloroformic phase is let down through a funnel, containing cotton wool and sodium sulpha in order to retain the dust-like floating particles, into second shaking funnel, containing 100 ml water and 1 ml 2M sulphuric acid. The extraction is repeated twice more wit 5 ml chloroform each time as described above. The 15 ml chloroformic solution of the esters is extracted with furt 3x100 ml water according to the above volumetric ratios in order to free it from butanol. The volume of the chloroformic solution of the esters becomes 25, 35 and 45 ml aft the second, third and fourth extraction steps, respectively In the course of the fourth, final extraction step the chloroformic solution of the esters is collected through a tulip funnel, containing cotton wool and sodium sulphate, into a 50 ml spherical flask and the sodium sulphate in th funnel is washed with 1 to 2 ml chloroform.

The chloroformic solution of the butyl esters is first concentrated to 2 to 3 ml in a vacuum rotary evaporator using room temperature water for heating, then the solution is quantitatively transferred into a 5 ml oval flask and concentrated to 0.3 to 0.4 ml and a 0.5 ml stock solution is prepared from it.

.1.1.3.2 Butylesterification of etheric extracts prepared from sulphuric acid digests

Half, i.e. 50 ml of the etheric extract of 1.5 g bauxite or red mud prepared according to para 3.1.1.3 is extracted in a 100 ml shaking funnel successively with 2 ml 0.2M and 3 times 2 ml 0.02M sodium hydroxide solution. The combined sodium hydroxide solution, containing the sodium salts of the carboxylic acids, is dried by evaporation in a water bath, then quantitatively washed with 1 to 2 ml distilled water into a 5 ml spherical flask in which it is dried by evaporation again. Then 0.1 ml distilled water and 0.3 ml butanol are poured into the flask and, after wetting the ground joint of the condenser with one drop of concentrated sulphuric acid, the latter is fitted on the esterifying flask, which is put in a hot water bath. Subsequently 0.2 ml concentrated sulphuric acid is introduced by means of a capillary tube reaching through the condenser into the flask. After at least 40 min esterification the procedure should be further carried out according to para 3.1.1.1.2 with the following differences:

- the ratio of distilled water to chloroform used for extraction should be 20 ml to 1 ml,
- the combined chloroformic solution of butyl esters filtered through sodium sulphate is concentrated by evaporation to 0.2 to 0.25 ml and a 0.3 ml stock solution is prepared from it.

3.1.2 DESCRIPTION OF THE GASCHROMATOGRAPHIC MEASUREMENT OF BUTYL ESTERS

3.1.2.1 Preparation of the column packing

An amount of support material corresponding to 1.5 times the volume of the column (CHROMOSORB W.A.W. D.M.C.S.) is weighed in a 500 ml spherical flask. A quantity of stationary phase Dexsil 300 G.C. calculated as 15 per cent of the solid support material is weighed with 0.01 g accuracy into a 200 ml beaker and dissolved in chloroform. After the complete dissolution of the stationary phase its chloroformic solution is poured on the support material. Should the chloroform containing the stationary phase not cover abundantly the support material, it has to be further diluted with chloroform. After letting it stand for 1 to 2 hours, while stirring the content of the flask repeatedly, the chloroform is quantitatively removed in a vacuum rotary evaporator. The column is filled from the glass bottle shown in Fig. 6 with the help of a water-jet vacuum pump. Both ends of the column are closed with glass wool pellets.

3.1.2.2 Preparation of the calibrating solution, containing n-butyl esters

5, 10 and 20 ml portions of the calibrating solution whose composition is detailed under the reagents of para 3. are pipetted with analytical precision into the butylesteri ing vessel and dried in a vacuum rotary evaporator after neutralization to pH 9 to 10. Subsequently 1 ml synthetic aluminate liquor and 3 ml butanol are introduced into the vessel, thereafter the procedure is carried out according to the prescriptions of para 3.1.1.1.2.

The esterification can be carried out from smaller quantities of the calibrating solution according to para 3.1.1.1.1, too. Taking into account, however, that the stock solution of n-butyl esters can be stored for an unlimited time in a well closed glass stoppered flask, the preparation of larger quantities is more expedient.

3.1.2.3 Separation of n-butyl esters

Separation of n-butyl esters of carboxylic acids ranging from formic acid to pyromellitic acid is carried out from 10 µl stock solution. High purity nitrogen is used as carrier gas with a flow rate of 10 ml per 10 to 15 s. Hydrogen is used at 0.2 bar, compressed air at 2 bar pressure. Chromatograms are prepared on the 2 and 3 m columns during 6 and 10 min, at 50 and 60 °C, respectively, under isothermal conditions. Subsequently the temperature is raised by 12 °C per min up to 350 °C. At this final temperature an isothermal elution of 5 to 10 min is required

3.1.2.4 Evaluation of n-butyl esters

When preparing the chromatograms the peaks corresponding to the main components, formic and acetic acids (in salt and alumina hydrate samples that corresponding to oxalic acid, too) are registered under our chromatographic conditions with a sensitivity of $S = 3.10^8$, those corresponding to the other components with a sensitivity of $S = 1.10^9$. The components of the calibrating solutions are characterized by carboxylic acid values expressed as integrator units per µg organic carbon. Quantities of known, examined components are calculated with the detector response of the corresponding carboxylic acid, unknown peaks with the average of the detector responses.

3.1.2.3 Retention order of carboxylic acid n-butyl esters

The retention order of carboxylic acid butyl esters is in Table 1.

Table 1.

RETENTION ORDER OF CARBOXYLIC ACID n-BUTYL ESTERS

Carboxylic acid butyl ester	Column 3 m x 4 mm	Column 2 m x 3 mm
	Retention time (s)	
Formic acid	460	353
Acetic acid	821	505
Di-n-butyl ether *	928	564
Propionic acid	1,021	596
i-Butyric acid	1,081	638
n-Butyric acid	1,144	680
i-Valeric acid	1,196	721
Oxalic acid	1,471	1,093
Benzoic acid	1,509	1,131
n-Butyl sulphate *	1,545	1,159
Succinic acid	1,601	1,250
Glutaric acid	1,664	1,320
Adipic acid **	1,728 **	1,391 **
Lauric acid **	1,732 **	1,395 **
Pimelic acid	1,785	1,448
Myristic acid	1,835	1,503
o-Phthalic acid	1,857	1,525
Palmitic acid	1,928	1,587
Stearic acid	2,016	1,696
Arachidic acid	2,116	1,784
Hemimellitic acid	2,136	1,805
Trimellitic acid	2,171	1,826
Trimesic acid	2,216	1,858
Behenic acid	2,244	-
Pyromellitic acid	2,310	2,112

* Evaluation is not disturbed by solvent-like products formed in various quantities in the course of esterification.

** Separately measured retention time of these carboxylic acids: they do not separate from each other in the course of simultaneous elutions.

3.1.2.6 Detector response of carboxylic acid n-butyl esters

Detector response of carboxylic acid butyl esters is shown in Fig. 7.

3.1.2.7 Details of evaluation of gas chromatograms

Qualitative and quantitative evaluation of the carboxylic acids present in the examined sample is made by means of the calibrating solution prepared from known quantities of carboxylic acids.

The evaluation can be made by hand or by a computer. The amounts of the individual carboxylic acid components are always expressed in organic carbon.

The basis of calculation is

- in case of computerized evaluation: integrator unit per µg carboxylic acid expressed in organic carbon,
- in case of manual evaluation (triangulation): carboxylic acid expressed in µg carbon per cm^2 peak area.

The method of calculation and evaluation is shown on the basis of chromatograms and tables prepared for butyl esters of the calibrating solution and a plant liquor (Figs. 8 and 9 and Tables 2 and 3).

The chromatogram showing the simultaneous elution of butyl esters of the calibrating solution and a plant liquor is presented in Fig. 10. In the course of computerized evaluation three numbers are ordered to each butyl ester peak:

1.) Retention time in seconds.
2.) The uncorrected integrator unit proportional to the quantity of the carboxylic acid.

3.) The corrected integrator unit proportional to the quantity of the carboxylic acid.

Experience shows that peaks corresponding to esters of acids from formic to oxalic, eluated on the falling branch of the curve, have to be evaluated by using the corrected integrator units, whereas for the evaluation of the other peaks the uncorrected integrator units have to be used. The mode of evaluation is of course a function of the performance of the integrator. Unknown components are calculated with the average of detector responses of known carboxylic acid esters (Tables 2 and 3).

It is noted, that the absolute detector response of the individual carboxylic acid butyl esters is a function of gaschromatographic conditions, first of all of the quality of the quartz nozzle used. The relative detector response of the individual carboxylic acid butyl esters is independent of the conditions and characteristic of the given carboxylic acid.

Table 2

CALCULATION OF THE DETECTOR RESPONSE OF THE AUTHENTIC CARBOXYLIC ACIDS ON THE BASIS OF FIG. 8.

Carboxylic acid butyl ester		Sensitivity	Retention time, s	Carboxylic acid in 10 μl solution expressed in org. C, μg	Computerized evaluation		Manual evaluation (triang.)		
Nr.	Name				total integrator unit	response*	total peak area, cm²	response**	
1	Formic acid	3.10^8	316.00	22.38	16,491	736.8	4.55	4.92	(1.48)
2	Acetic acid	3.10^8	668.40	34.80	42,631	1,225	6.60	4.27	(1.58)
3	Propionic acid	1.10^9	854.40	3.17	41,470	13,082	2.18	1.45	
4	i-Butyric acid	1.10^9	911.10	2.23	26,585	11,921	1.68	1.33	
5	n-Butyric acid	1.10^9	965.90	1.68	17,569	10,457	1.06	1.58	
6	i-Valeric acid	1.10^9	1,016.50	2.40	22,227	9,261	1.50	1.60	
7	n-Valeric acid	1.10^9	1,067.00	2.29	25,581	11,170	1.80	1.27	
8	Oxalic acid	3.10^8	1,301.40	7.29	13,419	1,840	2.80	2.60	(0.78)
9	Benzoic acid	3.10^8	1,328.50	3.22	3,714	1,153	0.70	4.60	(1.38)
10	Succinic acid	3.10^8	1,432.50	6.45	9,884	1,532	1.87	3.45	(1.03)
11	Glutaric acid	1.10^9	1,495.30	2.51	38,675	15,408	2.20	1.14	
12	Adipic acid	1.10^9	1,558.90	1.60	23,874	14,921	1.16	1.38	
13	Pimelic acid	1.10^9	1,617.90	0.98	12,140	15,564	0.36	2.16	
14	o-Phthalic acid	1.10^9	1,687.60	2.44	28,940	11.860	1.54	1.58	
15	Hemimellitic acid	1.10^9	1,943.10	0.44	9,799	22,270	0.22	2.00	
16	Trimellitic acid	1.10^9	1,976.70	1.39	10,197	7,335	0.32	4.34	
17	Trimesic acid	1.10^9	2,011.60	1.72	21,018	12,219	0.60	2.87	
18	Pyromellitic acid	1.10^9	2,269.00	1.72	6,982	4,059	0.18	9.55	
					Average:	12,444	Average:	2.15	

The chromatogram shown in Fig. 8 belonging to the table was prepared from 10 μl of the calibrating stock solution of the butyl esters on the 2 m column.

response*: integrator unit per μg carboxylic acid expressed in organic carbon
response**: carboxylic acid expressed in μg carbon per cm² peak area
Average: serves for evaluation of unknown butyl esters
responses in parentheses: values calculated for 1.10^9 sensitivity

Table 3

CALCULATION OF THE CARBOXYLIC ACID CONTENT OF A PLANT LIQUOR ON THE BASIS OF FIG. 9.

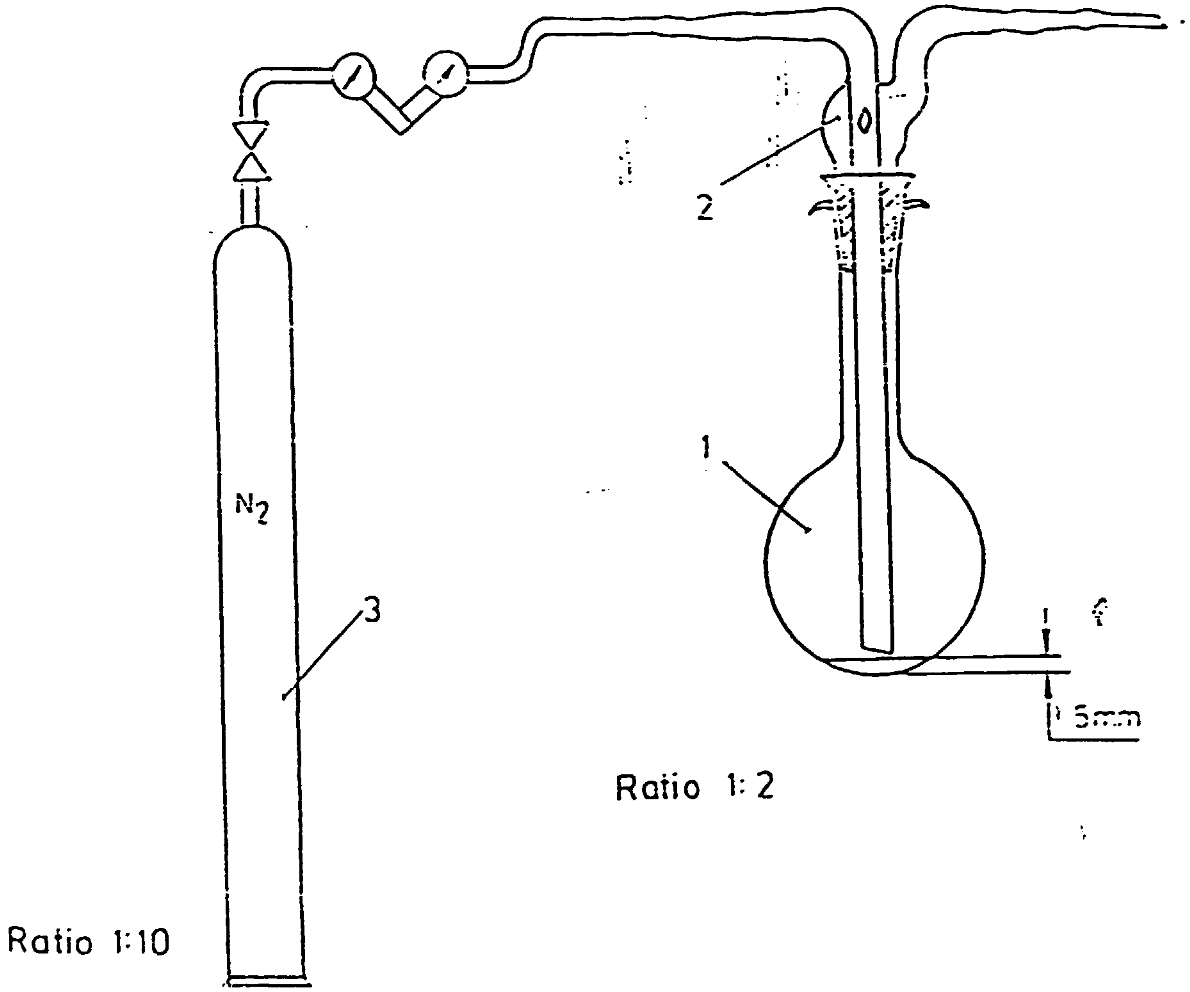
Carboxylic acid butyl ester Nr.	Name	Sensi- tivity	Retention time, s	Computerized evaluation			Manual evaluation (triangulation)		
				Carboxylic acid in 10 µl stock solution					
				integrator unit	ng expressed in org. C	in per cent*	peak area in cm²	ng expressed in org. C	in per cent*
1	Formic acid	3.10^8	305.0	14,999	20.36	13.60	3.81	18.74	12.50
2	Acetic acid	3.10^8	670.1	56,151	46.41	30.90	9.60	50.56	33.70
3	Propionic acid	1.10^9	853.2	33,494	2.56	1.70	1.90	2.76	1.80
4	i-Butyric acid	1.10^9	915.4	5,795	0.49	0.32	0.39	0.52	0.35
5	n-Butyric acid	1.10^9	968.9	5,580	0.53	0.36	0.32	0.51	0.34
6	i-Valeric acid	1.10^9	1,015.9	23,515	2.54	1.70	1.50	2.40	1.60
7	n-Valeric acid	1.10^9	1,077.8	496	0.044	0.03	0.04	0.051	0.03
8	Oxalic acid	1.10^9	1,306.2	57,748	3.14	2.10	3.84	3.00	2.00
9	Benzoic acid	1.10^9	1,337.6	3,718	0.32	0.21	0.105	0.15	0.10
10	Succinic acid	1.10^9	1,441.6	87,239	5.69	3.80	5.60	5.77	3.80
11	Glutaric acid	1.10^9	1,502.7	28,339	1.84	1.20	1.38	1.57	1.10
12	Adipic acid	1.10^9	1,564.3	8,843	0.59	0.40	0.37	0.51	0.34
13	Pimelic acid	1.10^9	1,619.2	18,080	1.16	0.77	0.57	1.23	0.82
14	o-Phthalic acid	1.10^9	1,689.1	39,883	3.37	2.30	2.29	3.62	2.40
15	Hemimellitic acid	1.10^9	1,948.1	12,524	0.56	0.37	0.32	0.64	0.42
16	Trimellitic acid	1.10^9	1,978.2	22,378	3.06	2.00	0.72	3.12	2.10
17	Trimesic acid	1.10^9	2,007.7	50,046	4.10	2.70	1.33	3.82	2.50
18	Pyromellitic acid	1.10^9	2,255.1	12,208	3.01	2.00	0.23	2.30	1.50
+	Other butyl esters			100,540	8.07	5.40	2.93	6.30	4.20
	Total:					71.90			71.60

The chromatogram of Fig. 9 belonging to the table was prepared from 10 µl of the 3 ml stock solution of butyl esters prepared from 5 ml plant liquor on the 2 m column.

* expressed in per cents of the total organic carbon

\+ not only pimelic acid

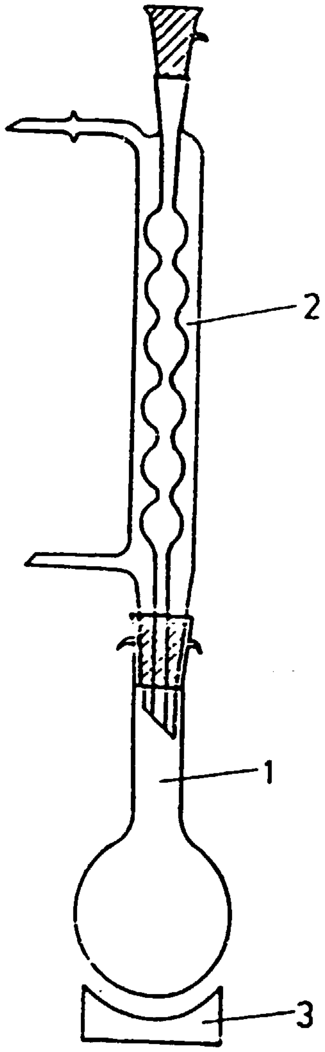
APPARATUS FOR THE ELIMINATION OF THE CARBON DIOXIDE CONTEN FROM ALUMINATE LIQUOR AND SODA SALT SAMPLES



1. Spherical flask
2. Gas inlet pipe
3. N_2 gas cylinder with reducer

Fig. 2.

APPARATUS FOR THE ELIMINATION OF THE CARBON DIOXIDE CONTENT FROM BAUXITE, RED MUD AND ALUMINA HYDRATE SAMPLES

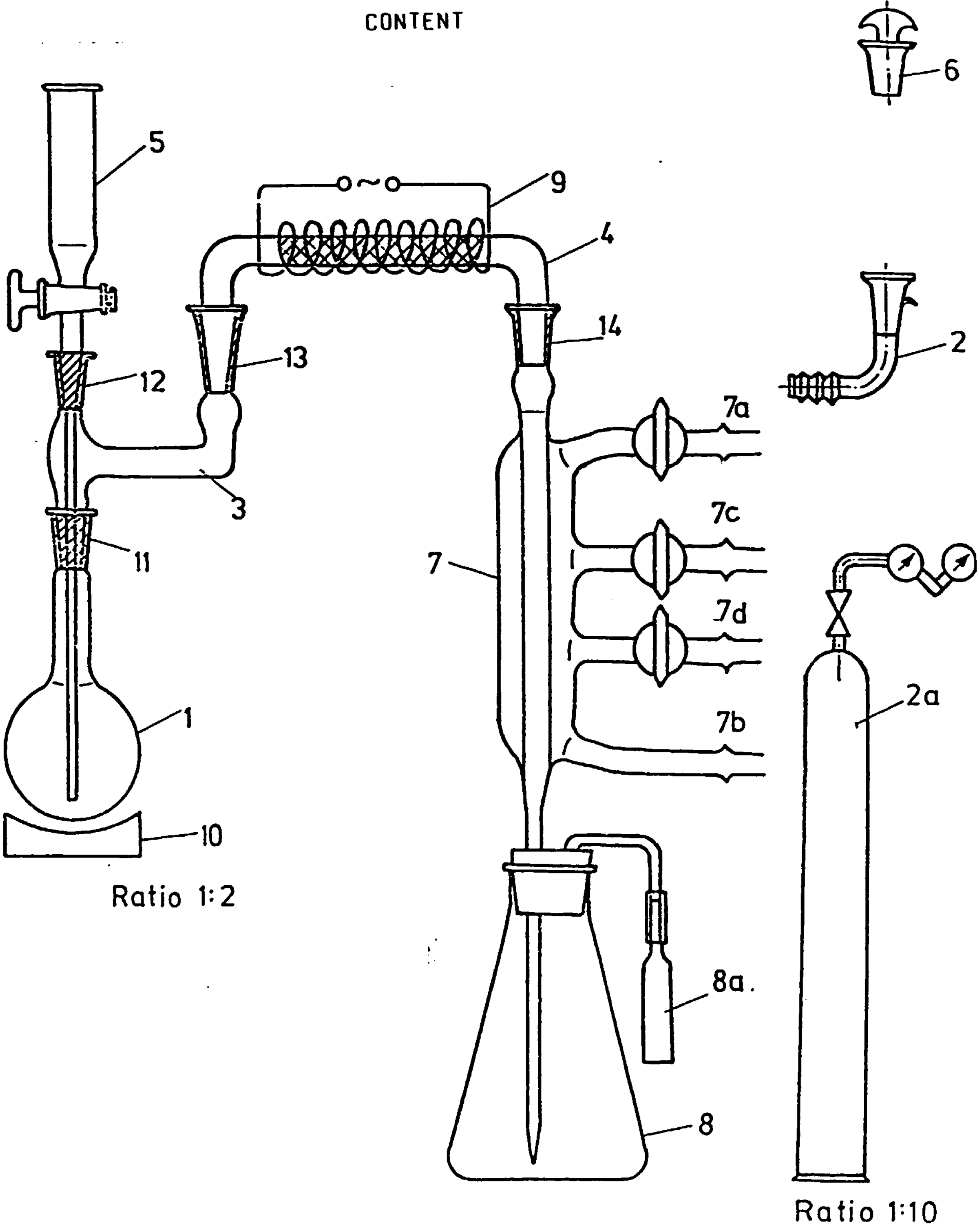


Ratio 1: 2.5

1. Spherical flask
2. Glass condenser
3. Hot plate

Fig. 1.

APPARATUS FOR DETERMINATION OF THE TOTAL ORGANIC CARBON CONTENT



1. Spherical flask
2. H_2 gas inlet pipe
2a. H_2 gas cylinder with reducer
3. Distributing pipe
4. Quartz pipe filled with copper wire
5. Feed funnel
6. Glass stopper
7. Cooler with water connections (7a, 7b, 7c, 7d)
8. Carbon dioxide absorption flask
8a. Glass tube filled with soda asbestos
9. Heating coil
10. Electric heater
11 to 14. Ground joints

Fig. 4.

BUTYLESTERIFYING VESSEL AND STIRRER

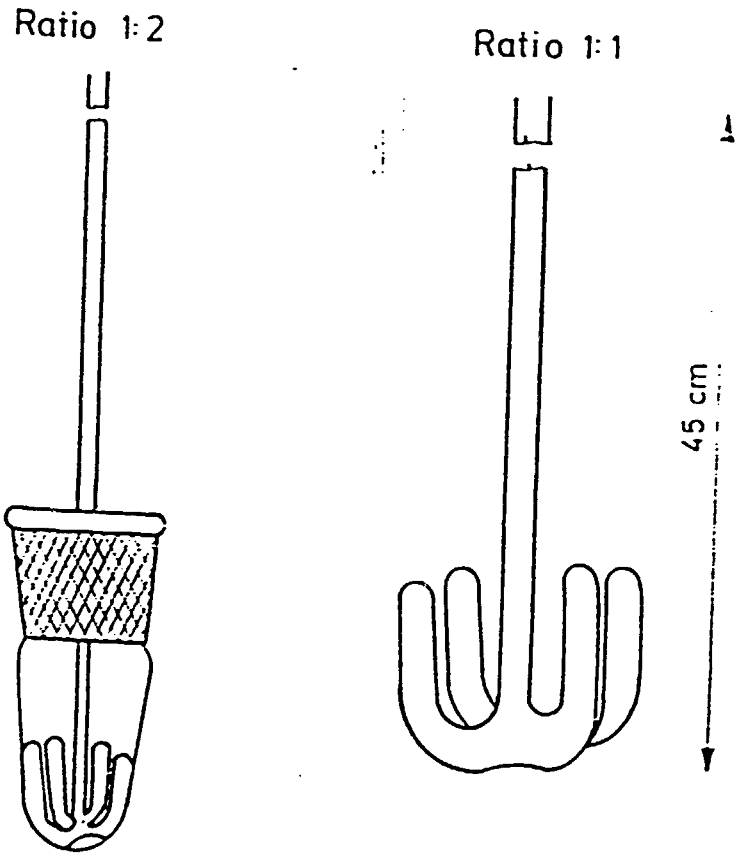
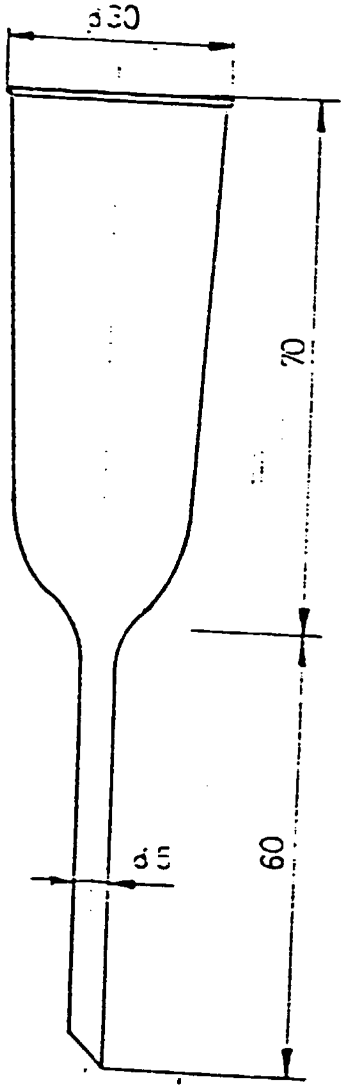


Fig. 5.

TULIP FUNNEL



Ratio 1:1