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On-Line Coupling of the MAT 251 with a Carlo Erba
Elemental Analyzer for Carbon Isotope Ratio
Measurements. Examples are Shown on Lake Sediments

Friedrich Pichlmayer

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WITH A CARLO ERBA ELEMENTAL ANALYZER
FOR CARBON ISOTOPE RATIO MEASUREMENTS.
EXAMPLES ARE SHOWN ON LAKE SEDIMENTS.

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ON-LINE COUPLING OF THE MAT 251 WITH A CARLO ERBA ELEMENTAL ANALYZER FOR CARBON ISOTOPE RATIO MEASUREMENTS.
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SUMMARY

For carbon isotope investigations with a moderate precision demand of about 0.2 per mil in the isotope ratio fast and reliable results are attained by on line combination of the ANA 1500 Elemental Analyzer and the MAT 251 Isotope Mass Spectrometer.

The crucial point hereof is the gas splitting device. By proper design and adjustment of the analytical parameters, good sample efficiency and a sharp CO₂ bulk within the He stream is reached.

The main characteristics of this combined equipment are described and some isotopic results of organic and anorganic carbon in lake sediment - samples are given as well as $\delta^{13}\text{C}$ -analyses of spiritous liquors.

In gas-isotope MS the basic idea of replacing the several cumbersome, mostly wet chemical preparation steps for the measuring gases N_2 , CO_2 and SO_2 by an universal digestion method is of course not new, and several papers are describing the on-line coupling of elemental analyzers with mass spectrometers.

The advantage of such a combination is the short overall cycle time of few minutes which make serial analyses economically possible. Also potential isotope discrimination sources during sample handling, for instance sample freezing, are avoided. The disadvantage is, that no use can be made of the full inherent MS - precision as comparison with the standard is only possible in sequential manner. In addition, δ -variations as function of sample amount, the so called pressure effect, may be of influence.

However, it will be shown in the course of this presentation, that with such an arrangement standard deviations of ± 0.1 to 0.2 ‰ are obtainable, which meets the precision demand of our lab, that applies isotope mass spectrometry in the fields of environmental and agricultural research.

In Fig. 1 the whole set up is shown. In principle the MAT 251 is fitted to the output of the Carlo Erba automatic nitrogen analyzer 1500 by means of a splitting device for the effluent He / measurement gas mixture. Additional equipment is a pyrometer for temperature measurement in the reaction furnace, a gasmonitor, for additional gas analyses by IR and by UV methods, the Spectra Physics Dual Channel Integrator SP 4270 for ion beam registration and a HP 3393 A Integrator for the TC detection of the chromatogram.

The left part of the schematically drawing (Fig. 2) comprises the elemental analyzer. Its main part is the quartz combustion reactor which is electrically heated to 1000 °C. A defined O_2 pulse of 5 or 10 ml is added to the He flow of about 1ml/sec by means of the injection valve. The weighed samples are contained in tin crucibles and dropped sequentially from the autosampler into the quartz furnace. At this moment flash combustion occurs and the temperature rises to max. 1700 °C ensuring quantitative

oxidation of the sample. The superfluous O_2 is retained by the copper and the reaction water is trapped subsequently in the H_2O trap. The produced measuring gases N_2 , CO_2 and SO_2 are carried by the He flow through the GC-column where they are separated from each other, and from possible byproducts, according to their different retention times. The concentration is measured by a thermal conductivity detector (TCD), calibrated with a concentration standard, on the other hand concentration measurement can be done by ion current detection which is more sensitive than the TCD.

The main function of the interface is to branch off a small but representative part, in our case about 1 - 0.1 % of the effluent and feed it to the mass spectrometer. In the literature higher splitting ratios are reported in order to drive smaller samples, but this causes higher vacuum pressure in the analyzer system and therefore loss of abundance sensitivity and deterioration of the plateau-shaped ion peaks due to small angle scattering. Because higher sample amounts are also necessary to obtain a sufficient sample to blank ratio, and that the unaltered MAT 251 capillary can be used, we decided to choose the quoted splitting ratio.

The interface consists essentially of the teflon tube connection, the appropriate designed branching T-piece and a forevacuum exhaust. The main effort was to obtain an as small as possible dead volume in the T-piece and to avoid alteration of the gasflow in the elemental analyzer in order to reach sharp CO_2 peak pulses within the He flow and therefore good integration conditions and short cycle time.

Experiments, carried out with different constructions and instrument parameters showed, that without evacuating the superfluous effluent, either disturbance of the gasflow or backdiffusion from the atmosphere occurs.

The mass spectrometer is driven at reduced emission current. Peak detection is performed preliminary by a Spectraphysics Integrator for reason of easy data processing, but it is intended to use the built in V/f converters in the future to get triple collector detection and therefore true ^{17}O correction.

In Fig. 3 the MS-background spectrum at the base pressure of 10^{-8} mbar and at He-influx, producing an analyzer pressure of 10^{-6} mbar (uncorrected) is shown. Due to He-impurities and out-gassing effects in the elemental analyzer, air constituents and the H_2O peak are enhanced. The carbon dioxide peak is roughly twice as high.

In Fig. 4 the ion currents of mass 44 and mass 45 are shown in the different cases: baseline, background at 10^{-8} mbar, He-inlet to 10^{-6} mbar, and the CO_2 bulk after combustion of 4 mg calcium carbonate. The signal is about 5000 times the He-inlet level, the signal to noise ratio is better $5 \cdot 10^4$. Both peaks are likewise shaped, their full width at half maximum is about 15 seconds. The ion peak appears 90 seconds after cycle start, the integration is performed over a period of 60 seconds. The He-inlet level is subtracted automatically. The carbon content of the tin container, which is typically in the low μg range, is of considerable influence on the resultant isotope ratio. The sample carbon should be therefore at least in the range of hundred μg , if the isotope ratios of blank and sample are too different.

The memory effect (Fig. 5) depends on furnace condition and is roughly one half of the blank contribution. Almost no CO_2 is produced in the cases of O_2 -inlet at $1000^\circ C$ furnace temperature. The Fig. 6 and 7 are printouts of tin crucible blank and NBS-20 samples. The tin container produces an ion signal of about hundredthousand counts in each channel, its carbon is approximately 20 % "lighter" than the carbonate carbon of the NBS-20. The signal area in this case is 20 million counts, the ion ratios of both NBS analyses are close together. Fig. 8 shows the corresponding NBS chromatograms. A small N_2 peak preceding the CO_2 can also be detected.

An important question is, whether the measured ion ratio depends on the sample amount. For detailed investigation, groups of measurements with different substances and different sample weights are performed. In the case of calcium carbonate (Tab. 1), the sample amount ranges between 1 and 8 mg. Each weight set consists of 7 individual samples. The external precision of them is shown in Fig. 9. No significant variation with sample weight could be observed. The maximum deviation is around ± 0.2 %.

Next, this on line technique was applied to carbon analyses of sediment samples. For the reason of possible carbon source identification in an Austrian freshwater lake, it is intended to analyze the isotopic composition of the sediments at different locations and depths. The measurements of such a depth profile are given in Tab. 2. The samplenumbers correspond to depths between 3 and 30 cm. The ion ratio and simultaneously the carbon content of total, inorganic and organic carbon were measured with six replicates.

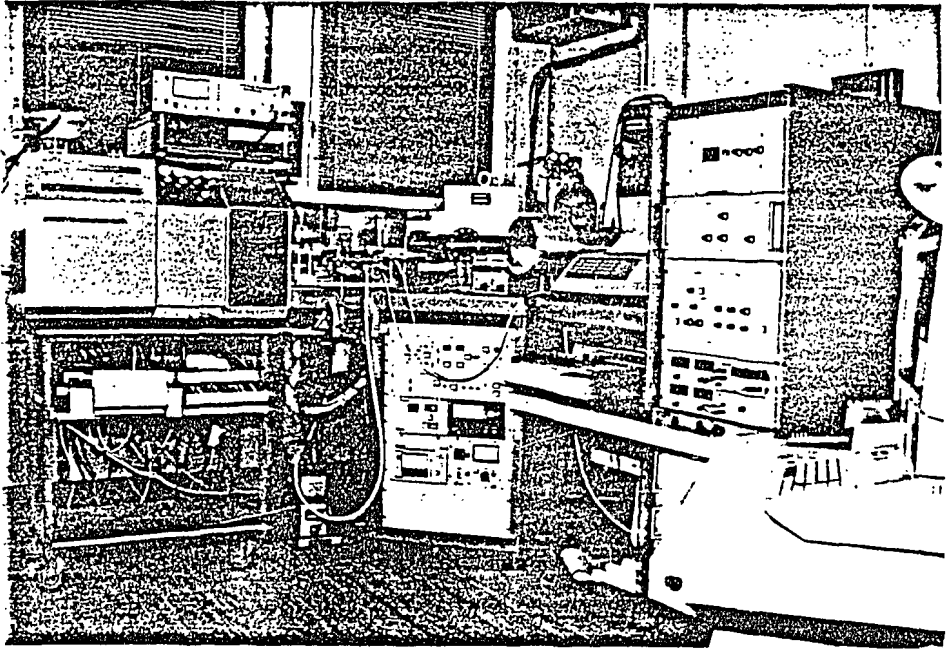
Before the inorganic carbon measurements, the organic species are removed by burning at 550 °C. In the case of organic analyses, the carbonates are removed previously by sample treatment with hydrochloric acid. The last sample is treated in both ways for procedure checking and therefore only a small carbon residue of about 6 µg remains.

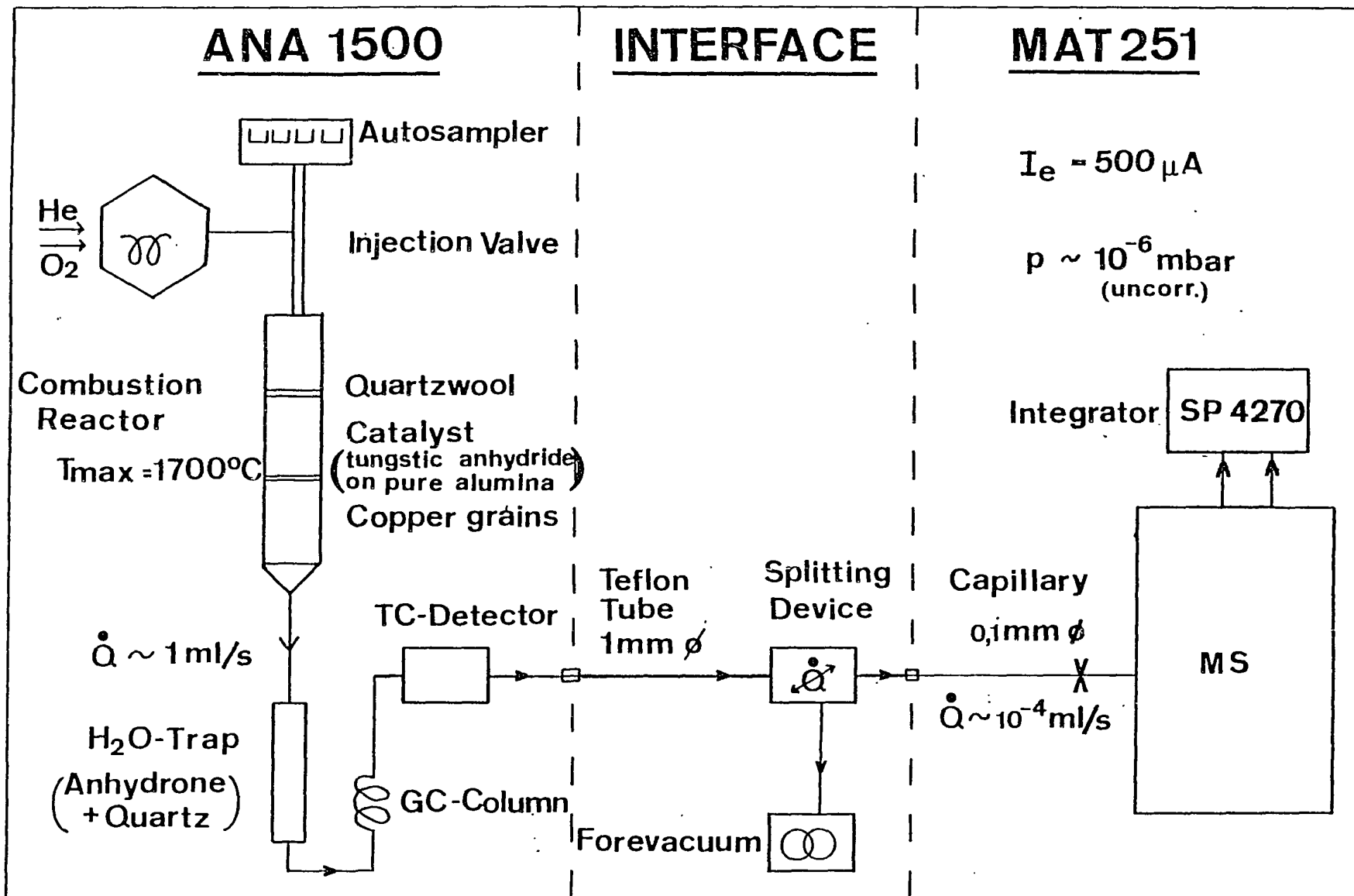
The ion ratios are transformed now to $\delta^{13}\text{C}$ values by means of NBS-20 measurements, assuming constant and normal ^{17}O content of the oxygen, and the results are given in Fig. 10. It can be noticed, that the C_{total} values are the very isotope mixture of organic and inorganic carbon, taking their different concentrations into account.

Finally, examples in the field of foodstuff-surveillance analysis are shown in Tab. 3.

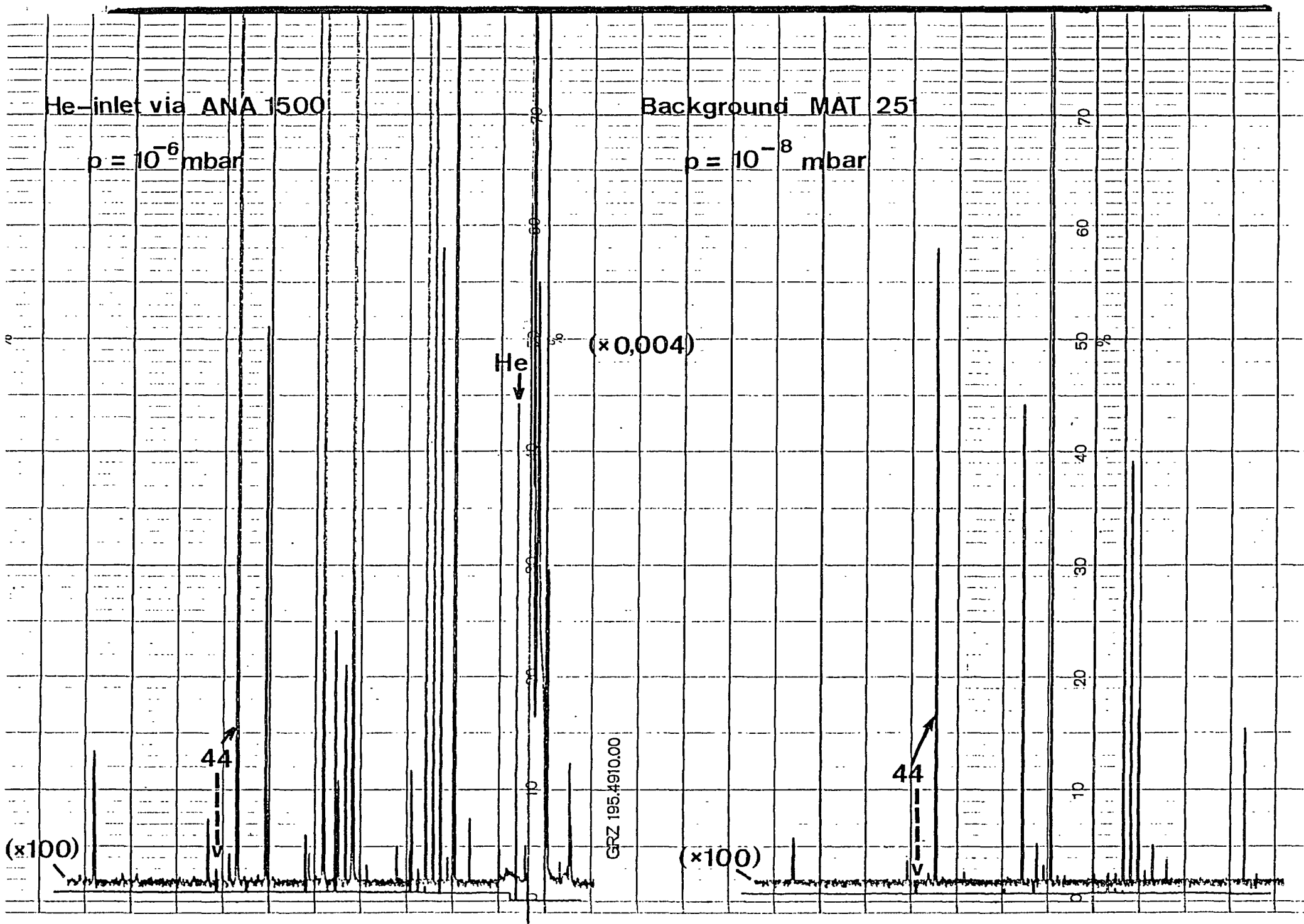
The most important application is the differentiation of $\delta^{13}\text{C}$ between the "heavy" C_4 -plants like maize or sugar cane and the "light" C_3 -plants which are the most other cultivated plants. Moreover, adulterations can be detected in certain cases. The listed spiritous liquors should all originate from C_3 -plants, which exhibits themselves small isotope variations.

One exception is the analyzed whisky, which is in fact a blend of grain- and maltwhisky. In the case of wine the adulteration with synthetic ethanol must be assumed.





SCHEME OF THE ELEMENTAL ANALYZER—MASS SPECTROMETER COUPLING



He-inlet via ANA 1500

Background MAT 251

$p = 10^{-6}$ mbar

$p = 10^{-8}$ mbar

He
↓

(x0,004)

44
↑
↓

44
↑
↓

GRZ 195.4910.00

(x100)

(x100)

m/z
70
60
50
40
30
20
10
0

10%
70
60
50
40
30
20
10
0

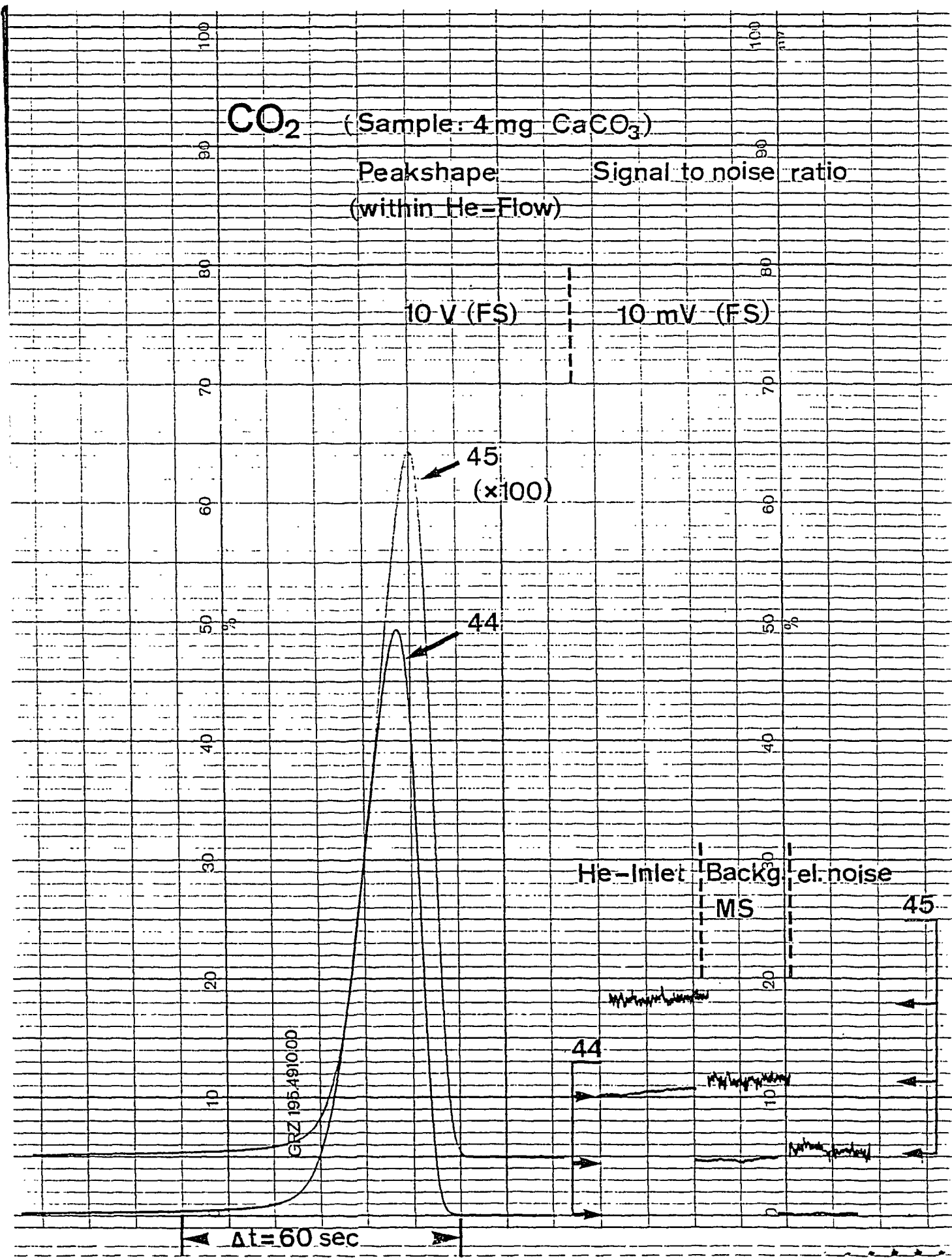



Fig. 4

END

CHANNEL A INJECT 20-02-86 10:35:10

 1.33

20-02-86 10:36:10 CH= "A" PS= 1.

FILE 4. METHOD 0. RUN 420 INDEX 420

PEAK#	AREA%	RT	AREA SC
1	100.	1.33	144002 01
TOTAL	100.		144002

← 45 - Signal (x100)

4.4 ERBA SCIENCE

20-02-86 10:36:11 CH= "B" PS= 1.

FILE 4. METHOD 0. RUN 430 INDEX 430

PEAK#	AREA%	RT	AREA SC
1	100.	1.32	121905 01
TOTAL	100.		121905

← 44 --Signal

R45/44 = 0,0118126

END

CO₂-BLANK: TIN CRUCIBLE

Fig. 6

1.86

27/05/86 13:12:33 CH= "A" PS= 1.

FILE	4.	METHOD	0.	RUN	119	INDEX	119
PEAK#		AREA%		RT		AREA	BC
1		100.		1.86		26393439	01
TOTAL		100.				26393439	

← 45 - Signal (x 100)

27/05/86 13:12:33 CH= "B" PS= 1.

FILE	4.	METHOD	0.	RUN	119	INDEX	119
PEAK#		AREA%		RT		AREA	BC
1		100.		1.85		16861443	01
TOTAL		100.				16861443	

← 44 - Signal
R45/44 = 0,0120947

1.84

27/05/86 13:17:57 CH= "A" PS= 1.

FILE	4.	METHOD	0.	RUN	120	INDEX	120
PEAK#		AREA%		RT		AREA	BC
1		100.		1.84		26821792	01
TOTAL		100.				26821792	

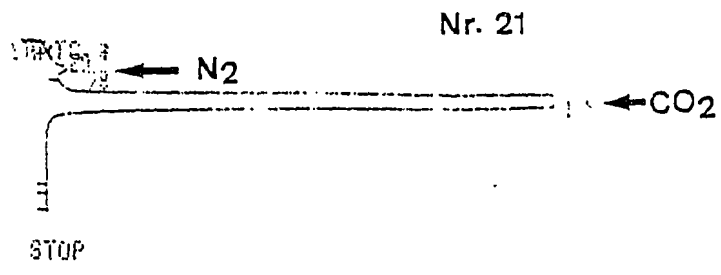
← 45 - Signal (x 100)

27/05/86 13:17:58 CH= "B" PS= 1.

FILE	4.	METHOD	0.	RUN	120	INDEX	120
PEAK#		AREA%		RT		AREA	BC
1		100.		1.83		17213723	01
TOTAL		100.				17213723	

← 44 - Signal
R45/44 = 0,0120960

CO₂: NBS 20 (~4mg)



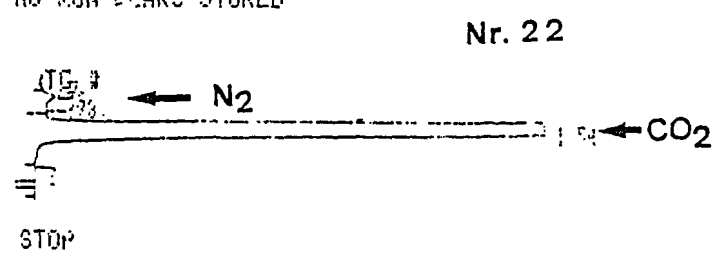
RUN # 29

RT	AREA	TYPE	AR/HT	AREA%
0.29	23053	PV	0.200	0.001
0.78	161160	WH	0.140	0.670
1.55	2.5202E+07	TSIH	0.204	99.329

TOTAL AREA= 2.5386E+07
MUL FACTOR= 1.0000E+00

STARTS # ?
STOP

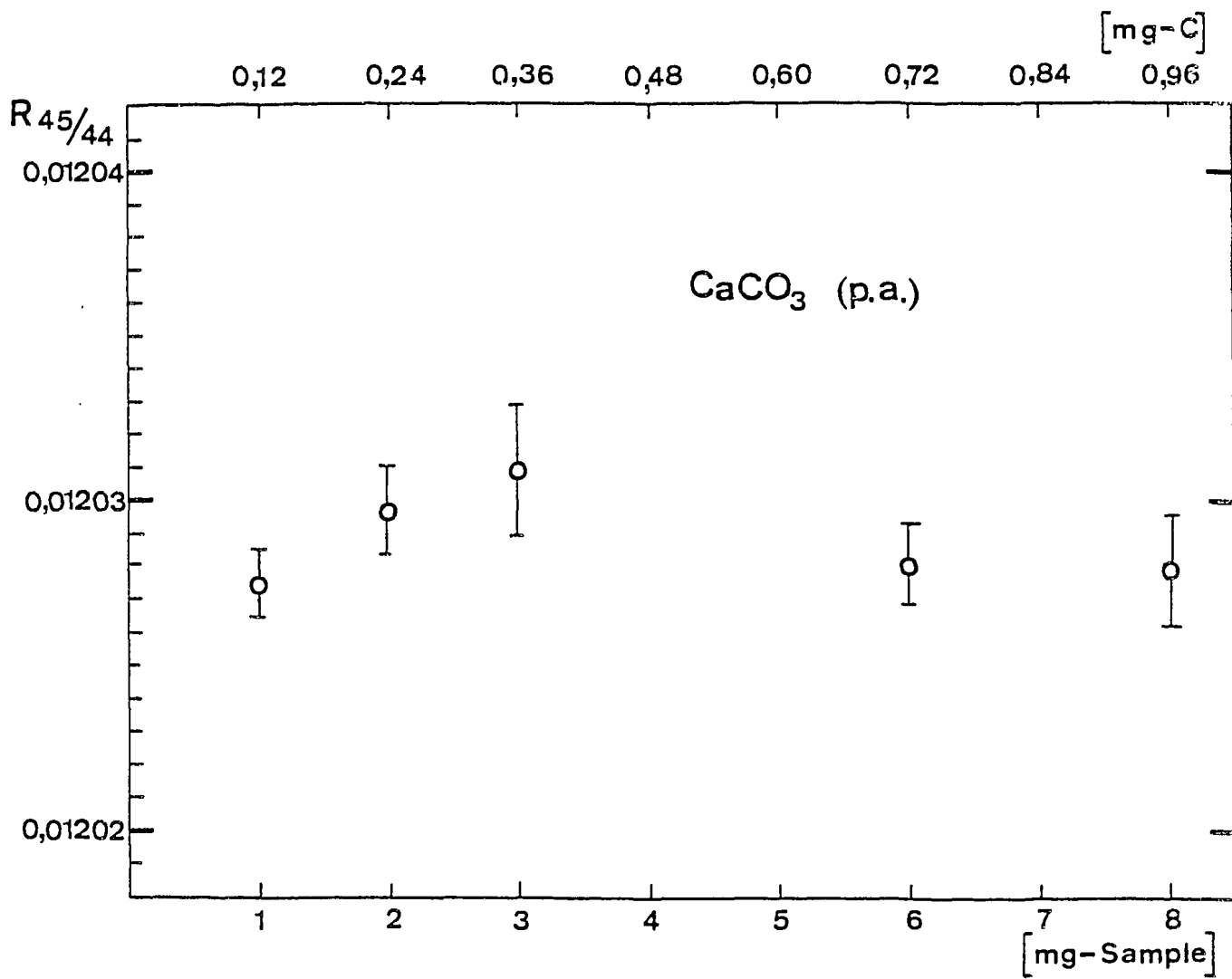
Run # 30
NO RUN PEAKS STORED



RUN # 31

RT	AREA	TYPE	AR/HT	AREA%
0.27	6225	PV	0.191	0.027
0.56	12704	VV	0.159	0.050
0.78	48606	VB	0.250	0.192
1.54	2.5271E+07	SPR	0.195	99.731

TOTAL AREA= 2.5339E+07
MUL FACTOR= 1.0000E+00



IONRATIO = f (sample amount)

Fig. 9

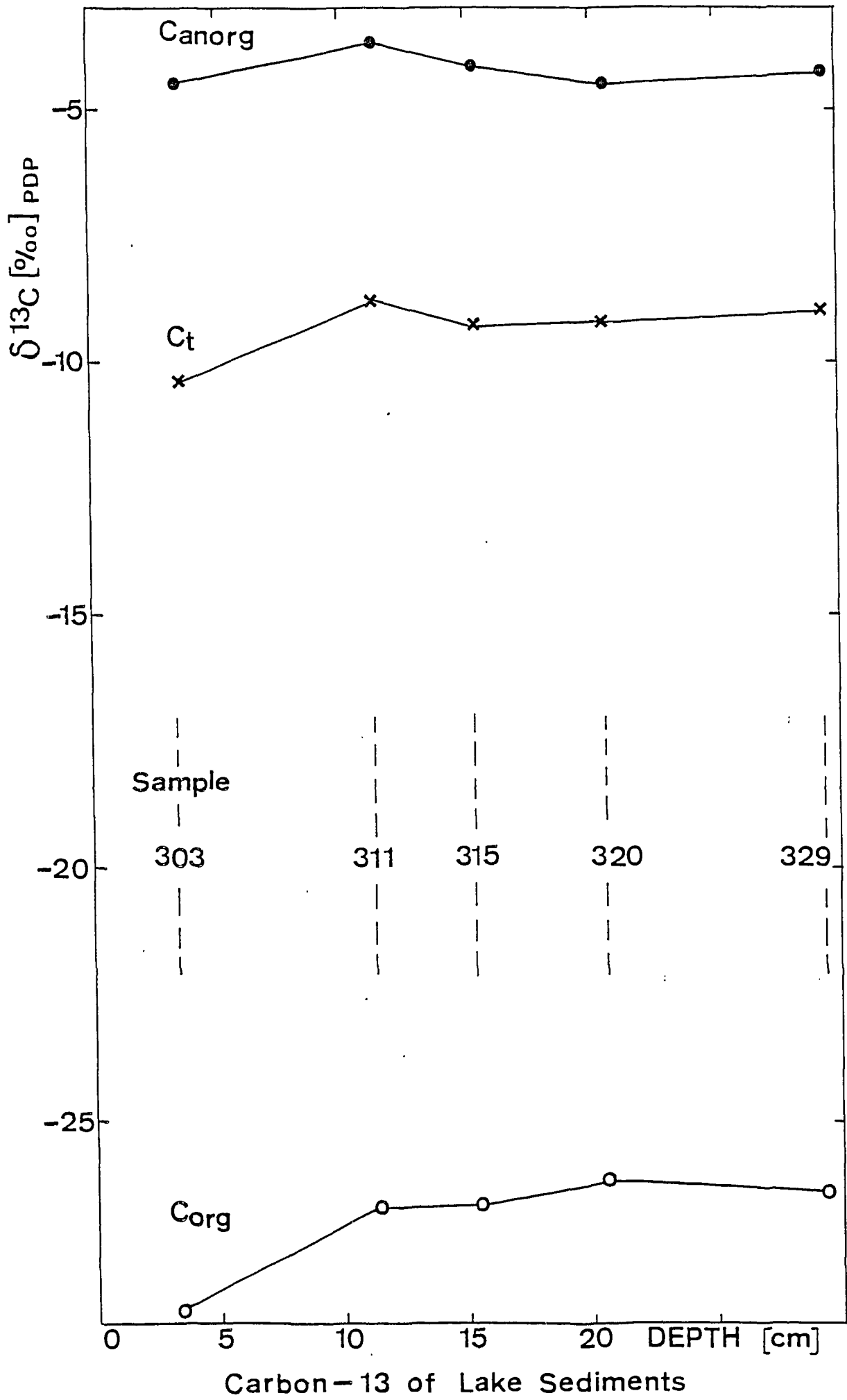


Fig. 10

Precision of ratio and variation of ratio
with sample amount

SAMPLE	NR.	EW (mg)	$R_{45/44} (x 100)$	
CaCO ₃	28	1,06	1,20263	
	29	1,06	1,20271	
	30	0,99	1,20288	
	31	1,05	1,20275	
	32	1,09	1,20269	
	33	1,10	1,20273	
	34	1,01	1,20288	1,20275 ± 10
	21	2,05	1,20289	
	22	2,00	1,20316	
	23	2,00	1,20310	
	24	2,07	1,20285	
	25	1,97	1,20283	
	26	2,12	1,20304	
	27	2,01	1,20293	1,20297 ± 13
	13	3,09	1,20300	
	14	3,05	1,20328	
	15	3,07	1,20284	
	16	3,00	1,20303	
	17	3,01	1,20289	
	18	3,05	1,20329	
	19	3,09	1,20329	1,20309 ± 20
	36	6,13	1,20276	
	37	6,37	1,20275	
	38	6,04	1,20300	
	39	6,35	1,20275	
	40	6,14	1,20264	
	40a	6,15	1,20292	
	40b	6,25	1,20285	1,20281 ± 12
	43	8,16	1,20263	
	44	8,00	1,20270	
	45	8,30	1,20279	
	46	8,35	1,20272	
	47	8,00	1,20283	
48	8,19	1,20273		
49	8,21	1,20314	1,20279 ± 17	

Ion ratio and carbon content of lakesediment samples
 (total carbon, anorganic carbon, organic carbon)

Nr.	sample weight (mg)	carbon	weight % C	R _{45/44} (x 100)
303	4	t	9,3	1,19636 ± 5
311	4	t	8,7	1,19821 ± 12
315	4	t	8,5	1,19762 ± 10
320	4	t	8,7	1,19765 ± 8
329	4	t	8,3	1,19803 ± 7
303	4	an (550 °C)	7,6	1,20346 ± 6
311	4	an (")	7,0	1,20441 ± 7
315	4	an (")	6,9	1,20381 ± 7
320	4	an (")	7,2	1,20341 ± 13
329	4	an (")	6,8	1,20368 ± 14
303	17	org (HCl)	2,1	1,17131 ± 22
311	20	org (")	1,7	1,17367 ± 3
315	18	org (")	1,7	1,17362 ± 5
320	17	org (")	1,7	1,17423 ± 12
329	18	org (")	1,6	1,17403 ± 35
315	4	res.org. (550 °C) + anorg. (+ HCl) (~ 6 µg C)	0,15	1,17955 ± 153

$\delta^{13}\text{C}$ results of some alcoholic liquors

	$\delta^{13}\text{C}$ (‰)
BARACK	$-24,3 \pm 0,1$
METAXA	$-23,7 \pm 0,1$
SLIVOVIC	$-24,2 \pm 0,1$
WODKA	$-22,8 \pm 0,1$
WHISKY (BLENDED)	$-17,2 \pm 0,1$
- GRAINWHISKY (MAIZE - C 4 :	$-10,9$)
- MALTWHISKY (BARLEY - C 3 :	$-24,2$)
BEER	$-25,1 \pm 0,1$
WINE	$-27,1 \pm 0,1$
<hr/>	
SYNTH. ETHANOL	$-31,0 \pm 0,1$
<hr/>	
STANDARD : NBS 22	$(-29,4)$

OEFZS-Berichte

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