FLAME IONISATION DETECTOR RESPONSE TO COELUTING HYDROCARBONS AND CARBON DISULPHIDE AND ITS APPLICATION TO THE DETERMINATION OF THE SUM OF C_6—C_{11} ALKANES AND CYCLOALKANES IN AIR

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The flame ionisation detector response to C_6—C_{11} aliphatic hydrocarbon solutions in carbon disulphide in the concentration range between $1·3$—$9·5$ mg ml^{-1} retained linearity despite the excess of solvent entering the detector simultaneously with the analyte. Pure carbon disulphide exhibited a small positive detector response which did not interfere in calibration procedure and which, under certain GC conditions, inverted to negative values. This response was not proportional to the injected volume and was strongly influenced by the column temperature and/or bleed. On the basis of these findings, a method compatible with the widely used charcoal tube carbon disulphide desorption procedure was developed and evaluated. It consists of static desorption of the sum of aliphatic alkanes and cycloalkanes from the activated charcoal after which an internal standard is added to the supernatant eluate. The resulting carbon disulphide solution is analysed on a highly polar stationary phase 1,2,3-tris(2-cyanoethoxy)propane where the solvent and the analyte coelute in a single peak, the height of which is practically proportional to the sum of alkanes and cycloalkanes present. This also makes determinations of other substances present in the sample more simple. The field test of the proposed method yielded values comparable in precision and accuracy with a control infrared spectrophotometric method.

In the industrial hygiene practice, the determination of the sum of alkanes and cycloalkanes (SAC) in air is usually carried out using turbidimetry[1,2], nephelometry[3,4], infrared (IR) spectroscopy[5], gas chromatography (GC) (ref.[6-9]) or gravimetry[10,11]. All these methods attempt, more or less successfully, to achieve the determination of SAC as a class of compounds because hygienic threshold limit values (TLV) usually do not distinguish among isomeric alkanes nor among individual aliphatic hydrocarbons (approximately C_6—C_{11}).

The main obstacle in the GC determination of the SAC is the fact that, unless a highly polar stationary phase is used, the more or less complete separation of analysed isomeric and homologic alkane mixtures takes place. One possibility of solving this problem is the integration of the area of incompletely resolved peaks[6-9]. However, this method is tedious and prone to interference from coeluting nonhydrocarbon substances and it also requires a good baseline stability.

The use of a highly polar stationary phase for the GC group separation of saturated hydrocarbons is not new[12-15]. While a single peak can be readily obtained in this way for isomeric and homologic alkane mixtures, the shape of this peak is often asymmetric and resembles the distribution of respective elution times for individual components. For the most precise results, the peak area integration should be employed but the peak height measurement also yields results of acceptable precision.

Nevertheless, in connection with the widely used activated charcoal (AC)/carbon disulphide (CD) desorption procedure[16] a new problem is encountered as CD coelutes with the SAC peak and is burnt in a large excess in the flame ionisation detector (FID) flame simultaneously with the analyte. Although the FID response mechanism to hydrocarbons and their derivatives was studied thoroughly in the past[17] and while it was a subject of some excellent reviews[18-20], no information has been available so far about the influence of coeluting CD on the FID response to hydrocarbons. Serious doubts were voiced[21] as to whether the FID linearity would be retained under such extreme conditions. Literary data gives only incomplete picture as in the work[22] some influence of CD on the FID response to methane was noted while in the earlier work[23] the addition of sulphur dioxide or hydrogen sulphide to a coal gas fed into a FID did not alter the response. Other related studies concentrated mainly on the FID response to CD only[24-27].

The aim of this work was to investigate the linearity of the FID response to C_6-C_{11} alkanes and cycloalkanes coeluting with CD and to develop and evaluate the method for the determination of the SAC at concentration levels encountered in the industrial hygiene inquiries using highly polar stationary phase 1,2,3-tris(2-cyanoethoxy)propane (TCEP) in connection with the previously described modified AC/CD desorption procedure[28].

EXPERIMENTAL

Materials and Reagents

Analytical grade carbon disulphide (Merck, Federal Republic of Germany) was used without further purification. Pure toluene (Lachema Brno, Czechoslovakia) and p-xylene (Reachim, USSR) were used after a brief GC check for impurities without further purification. Technical gasoline (distillation range 353—383 K) and white spirit (distillation range 413—473 K) samples were used as received from a local office of the petroleum derived products distributor (Benzina). The sulphuric acid/formaldehyde reagent test for a possible presence of trace amounts of aromatics was positive. As trace aromatics did not interfere significantly in the course of the work, no attempts were made to purify these samples.

Samples of copying fluids for zinc oxide electrostatic photocopiers (Fomastatic, Fomastatic NDF, Fotochema Hradec Králové, Czechoslovakia) which were, as confirmed by IR spectroscopy, mixtures of aliphatic hydrocarbons, were obtained at random in various copying offices as supplied by the manufacturer. Only the Fomastatic NDF fluid samples gave positive tests for traces of aromatics.

Glass sampling tubes (4 mm i.d.) of the previously described construction[28] were used with one or two layers (135 mg $\pm$ 10%) of the HS 1 activated charcoal (Hrušovské chemické závody, Ostrava, Czechoslovakia, particle size 0·5—1·0 mm) retained by open pore polyurethane foam plugs[29].

Commercial GC columns packings wer used (Lachema) employing 0·20—0·25 mm Chromaton N-AW-DMCS diatomite support coated with 10% of TCEP or DC 550 stationary phase.

The electric bulb grade nitrogen was used as the carrier gas without purification. The hydrogen for FID operation was also used without purification as received or was supplied from an electrolytic generator (General Electric, USA). The air for FID was supplied either using an aquarium membrane pump, in which case it was purified by a passage through an AC column, or from a pressure cylinder.

Apparatus

Gas chromatograph Chrom 31 (Laboratorní přístroje, Prague) equipped with the polarized jet type FID (jet negative) and stainless steel columns (1·2 m $\times$ 6 mm i.d.) containing about 13 g of packing. Gas flows were usually set as follows: carrier gas 65—80 ml min^{-1} (at the column inlet, p_i from 55 to 75 kPa), hydrogen 50—60 ml min^{-1}, air 1·0—1·1 l min^{-1}. This instrument will be referred to as instrument A.

Gas chromatograph Chrom 41 (Laboratorní přístroje, Prague) equipped with a stainless steel column (1,2 m $\times$ 3 mm i.d.) packed with 3·7 g of the TCEP packing. The FID of this instrument is of a semicylindrical construction using two opposite insulated semitubular parts as polarizing and collecting electrodes. Approximate values of gas flows were as follows: carrier 35—45 ml . . min^{-1} (at the FID jet), hydrogen 35 ml min^{-1}, air 400—420 ml min^{-1}. This instrument will be referred to as instrument B.

In the course of this work 1 µl injections were routinely used except the CD response study when as much as 4 µl were injected. In these cases, the odour of the sulphur dioxide could be clearly smelt around the instrument and, when repeated several times, quick deterioration of the FID performance usually took place. A thorough cleaning of the detector insulation and electrodes was then neccessary to restore the original operating condition.

Test atmospheres were prepared using the experimental setup and permeation devices of the previously described construction[28,30] and concentrations of permeants were adjusted to approximate TLV value for the technical gasoline which is 0·5 g m^{-3} in Czechoslovakia.

FID Response Linearity Study

For the study of the FID response to hydrocarbons coeluting with the excess of CD three sets of solutions were prepared and final concentrations with other details are given in Table I.

Solutions thus obtained were analysed by GC, each sample being analysed four times at four different column temperatures on both instruments except Fomastatic NDF solutions which were analysed on instrument A only. Chromatograms were evaluated by measuring peak heights and, after calculating peak height ratios $h_{analyte}/h_{internal\ standard}$, resulting values were averaged and regression lines were calculated using analyte/internal standard (IS) concentration ratios as independent variables. Results of these calculations are summarized in Table II.

To check the possible peak height ratio dependence on the injected volume, technical gasoline and white spirit samples were analysed four times again at four column temperatures, the injection volume being changed from 1 to 4 µl. Calculated peak height ratio averages were then plotted against injected volumes as shown in Fig. 1.

The FID response to CD was studied on instrument A at three different column temperatures using both TCEP and DC 550 columns. Resulting peak shapes are shown in Fig. 2.

FID Ionisation Efficiency Study

In order to check whether the FID ionisation efficiency for analysed alkane mixtures is to any extent affected by the CD presence in the FID flame, solutions of technical gasoline in CD (4·49 mg ml^{-1}) and in p-xylene (4·18 mg ml^{-1}) and of white spirit in CD (4·86 mg ml^{-1}) and in p-xylene (4·50 mg ml^{-1}) were prepared and analysed without the IS addition on instrument A
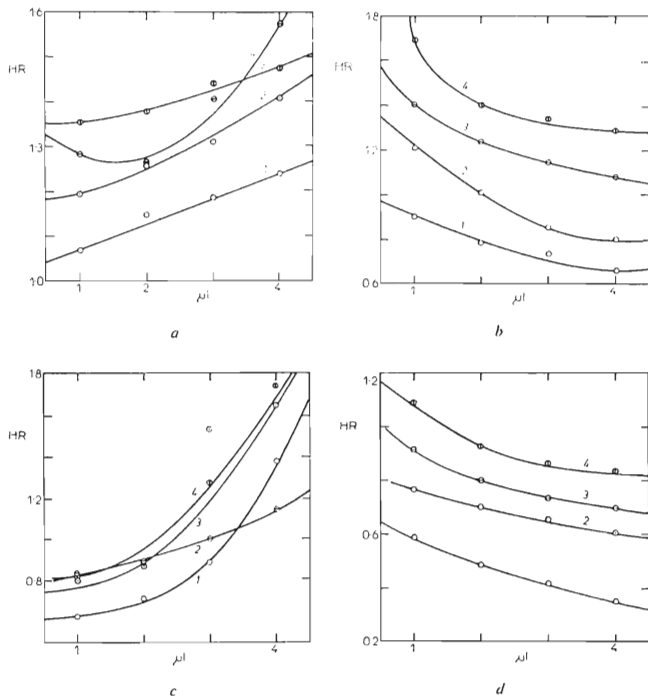

FIG. 1

Peak height ratio (HR) as a function of the sample volume injected at various column temperatures. Analyte concentration: technical gasoline 3,9 mg ml^{-1}, white spirit 5,7 mg . ml^{-1}, concentration ratios $c_{analyte}/c_{IS}$ 0·49 (technical gasoline), 2·98 (white spirit). a: Technical gasoline, instrument A, 1 405 K, 2 389 K, 3 374 K, 4 358 K. b: White spirit, instrument A, 1 420 K, 2 405 K, 3 390 K, 4 374 K. c: Technical gasoline, instrument B, 1 404 K, 2 388 K, 3 373 K, 4 358 K. d: White spirit, instrument B, 1 421 K, 2 404 K, 3 388 K, 4 375 K

using the TCEP column. In this case, the peak heights were compared directly after corrections for concentration differences. As for p-xylene solutions the analyte eluted well before the solvent peak, the FID operation was considered to be unaffected by the solvent in these cases.

Desorption Efficiency Determinations

To obtain some additional information on desorption efficiency (DE) values to those reported previously for n-heptane and cyclohexane[28], the same procedure as described in[28] was applied to technical gasoline, white spirit and Fomastatic NDF samples. The only differences were that two samples were prepared for 5, 10 and 40 minutes sampling periods beside five standard samples

TABLE I

Analyte solutions

Analyte	c_{anal} range[a] mg ml^{-1}	c_{IS}[b] mg ml^{-1}	c_{anal}/c_{IS} range[a]
Technical gasoline	0—6·5	8·0	0—0·81
White spirit	0—9·4	1·9	0—4·97
Fomastatic NDF	0—9·2	4·0	0—2·31

[a] In six equidistant steps; [b] p-xylene except for technical gasoline where toluene was used as the internal standard; c_{anal} analyte concentration; c_{IS} internal standard concentration.
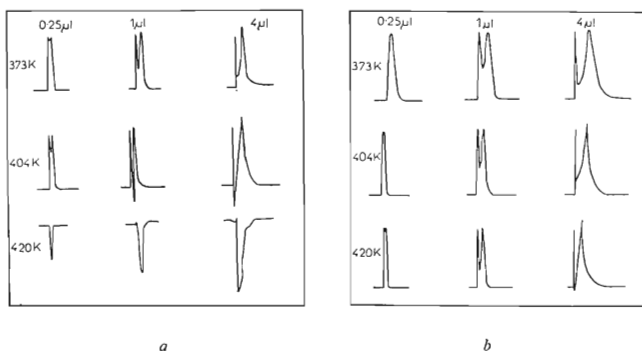

FIG. 2

Influence of the injection volume and the column temperature on the CD peak shape. a: Instrument A, TCEP column. b: Instrument A, DC 550 column

(20 min) at the 0·5 l min^{-1} sampling flow. No breakthrough was noted for 40 min sampling periods as confirmed by backup layers analyses results.

TABLE II

Linear least squares calculation results for the peak height ratio dependence on the analyte/internal standard weight ratio

Column temperature K	r_{xy}	t_{b_0}	$b_0 \cdot 10^2$	b_1	$s_R \cdot 10^2$	$s_{b_0} \cdot 10^2$	$s_{b_1} \cdot 10^2$
Light gasoline, instrument A, internal standard concentration 8·020 mg ml^{-1}							
359	0·9994	2·71	6·681	2·798	3·4020	2·4622	5·0170
374	0·9991	2·93	7·803	2·493	3·6795	2·6630	5·4263
389	0·9997	3·87	5·228	2·308	1·8668	1·3511	2·7530
404	0·9998	4·80	4·715	2·126	1·3579	0·9827	2·0025
Light gasoline, instrument B, internal standard concentration 8·020 mg ml^{-1}							
358	0·9997	0·45[a]	0	1·672	1·3215	—	1·0993
374	0·9986	0·60[a]	0	1·593	2·6559	—	2·2093
388	0·9980	0·91[a]	0	1·582	3·2926	—	2·7389
403	0·9906	1·06[a]	0	1·813	9·1328	—	7·5972
White spirit, instrument A, internal standard concentration 1·898 mg ml^{-1}							
374	0·9998	29·31	40·03	0·4363	1·8871	1·3657	0·45402
390	0·9997	18·20	23·69	0·3859	1·7989	1·3020	0·43282
405	0·9988	6·47	16·41	0·3383	3·5051	2·5369	0·84331
420	0·9907	1·78[a]	0	0·2956	11·222	—	1·5230
White spirit, instrument B, internal standard concentration 1·898 mg ml^{-1}							
375	0·9983	2·06[a]	0	0·3507	5·2757	—	0·71599
388	0·9994	0·90[a]	0	0·3008	54·880	—	7·4481
404	0·9998	7·98	−7·227	0·2832	1·2509	0·90531	0·30096
421	0·9993	8·54	−10·96	0·2313	1·7743	1·2841	0·42688
Fomastatic NDF, instrument A, internal standard concentration 4·002 mg ml^{-1}							
373	0·9987	4·24	12·20	0·8209	3·9751	2·8770	2·0590
388	0·9997	4·25	5·489	0·7884	1·7848	1·2917	0·92446
403	0·9974	0·31[a]	0	0·5646	3·6227	—	1·0585
419	0·9820	2·93	−17·15	0·4355	8·0813	5·8489	4·1859

[a] Intercept value not significantly different from zero ($\alpha = 0·05$); r_{xy} coefficient of correlation; t_{b_0} intercept t-test value; b_0 intercept; b_1 slope; s_R residual standard deviation estimate; s_{b_0} intercept standard deviation estimate; s_{b_1} slope standard deviation estimate.

In order to asses whether it is neccessary to take the FID response to CD into account, two sets of calculations were performed, namely one using the previously described procedure[28] based on a single calibration solution (equivalent thus to the zero intercept assumption) and another using the linear regression calculation and a set of calibration solutions for the quantitation of results. These will be called single point and multipoint approach, respectively. DE measurement results for standard samples were then subjected to the single factor analysis of variance (ANO-VA)[31] and can be found in Tables III and IV. All DE values were obtained using instrument A.

Field Test of the Proposed Method

To check the practical utility of the proposed procedure in a real situation, paired samplings were performed at various photocopying offices of the concentration of Fomastatic NDF fluid vapours in air. Then the proposed method for the determination of SAC, consisting of the static desorption of the adsorbed SAC from AC with 1 ml of CD and analysing the eluate using IS and TCEP column, was applied to one of each pair of samples. The single point approach was used for the quantitation of results in all these cases. The other sample from the pair was worked up by desorption with 5 ml of tetrachloroethylene followed by the transmittance measurement at 2 930 cm^{-1} against the solvent blanc in 0·5 cm quartz cuvettes[5]. In some cases IR transmittances of portions of CD eluates were also measured using a KBr window cell (0·1 or 0·27 mm) against the CD blanc. In these cases SAC concentrations in samples were calculated using respective calibration graphs.

Paired results obtained this way were plotted and the equation of the regression line was calculated as shown in Fig. 3.

DISCUSSION AND RESULTS

FID Response to Carbon Disulphide

Findings presented in this work can be, to some extent, compared easily only to results from[24] where 1 µl injections were employed whereas in other works on this subject
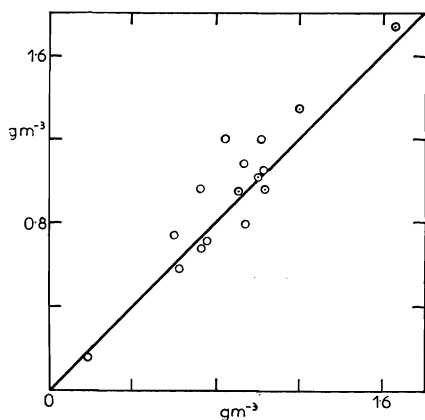

FIG. 3

Correlation of field sampling results obtained by the GC procedure described (single points approach, DE value of 107% used) and by the control IR method. ○ Gc, $n = 16, r_{xy} = 0.9294$. ⊙ IR, results obtained from CD eluates, $n = 5, r_{xy} = 0.9781$

TABLE III
ANOVA results for standard samples desorption efficiency determinations (20 min sampling period) calculated using the single point approach

Values	Cyclohexane[a]	n-Heptane[a]	Technical gasoline	White spirit[b]	Fomastatic[b] NDF
Load, mg	5,23	5·72	5·23	6·57	4·91
DE value, %	101·1	106·8	107·5 (112·3)[c]	93·5 (92·8)[c]	106·8 (87·9)[c]
SS_{tot}	539 588	1 882 314	313·668	150 000	230 100
MS_{among}, $\nu_{among} = 4$	60 008	311 305	44 022	7 244	10 210
MS_{res}, $\nu_{res} = 15$	19 970	42 451	9 172	8 068	12 617
F	3·01	7·34	4·80	1·11	1·24

Instrument A and the TCEP column at 373 K were used for all determinations except where noted otherwise. [a] taken from[28]; [b] column temperature 388 K; [c] calculated using the multipoint approach; ν degrees of freedom; DE desorption efficiency; SS_{tot} total sum of squares; MS_{among} mean squares among samples; MS_{res} residual mean squares; F calculated test value.

dosed amounts ranged from about 3 μg in[23] to 630 μg in[26] (2 − 500 ml) with the region studied most extensively between 48 and 228 μg (38 − 180 nl)[25,27].

Chromatograms obtained in the present work for the pure CD resembled closely those given in[23] and [32] (Fig. 2). To check whether a response inversion resulting in a notch in the detected peak such as shown in Fig. 2 could be caused by the excessive column bleed (the upper temperature limit for the TCEP stationary phase is about 420 K, the background current was about 1,7 nA at this temperature, the same set of analyses was run using the DC 550 column which offered much lower bleed (0,25 nA at 420 K). It can be seen that the lower column bleed and consequently lower background current led to a decrease in the size of the notch on the CD peak when compared to the TCEP column. The peak current at which the response inversion occurred was remarkably constant amounting, after the correction for the background, to about 0,5 nA for the DC 550 column.

These findings are consistent with the dichotomous process explaining the inversion of the FID response to CD given in[22] consisting of the ionic species formation and of the inhibition of the former by sulphur fragments.

TABLE IV

The effect of the varying load on the desorption efficiency values

Sample	Sampling period min	load mg	DE, %[a]	DE, %[b]
Technical gasoline	5	1·31	113·8	84·8
	10	2·62	111·7	105·6
	20	5·23	107·5	112·3
	40	10·46	98·1	107·2
White spirit	5	1·64	115·5	84·8
	10	3·28	102·4	97·9
	20	6·57	93·5	92·8
	40	12·98	81·2	85·6
Fomastatic NDF	5	1·23	112·7	73·1
	10	2·45	105·0	78·8
	20	4·91	106·8	87·9
	40	9·81	103·7	88·5

Values were determined using instrument A at conditions listed in Table III. All results are averages from two determinations oxcept for 20 min sampling periods where results are averages from five determinations. [a] Calculated using the single point approach; [b] calculated using the multipoint approach.

The reason for the different CD behaviour on TCEP and DC 550 columns can be, besides differences in bleeding characteristics, also a stronger retention of CD on the less polar DC 550 column when compared to the highly polar TCEP stationary phase This would lead to a more gradual introduction of the CD into the FID flame due to the peak spreading, extending thus the time when FID is still working in the "normal" region[22], while for high column temperatures and the less retentive TCEP column, the steep leading edge of the CD peak would almost instantaneously bring the FID into its "anomalous" part of the response curve[22]. The high background current would in this case also facilitate a strong negative response.

FID Ionisation Efficiency Study

When corrected for concentration differences, technical gasoline solutions in CD and *p*-xylene gave different responses as indicated by the *t*-test value of 4,65 ($v = 34$) but the difference amounted only to 12—13%, the response being higher in the case of the CD solution. Such difference can be easily explained only on the basis of different volatilities of solvent used.

For white spirit solutions, the difference was also statistically significant ($t = 25.5$; $v = 19$), this time the CD solution response being about 39% lower. Peak shapes were markedly asymmetrical in this case with well developed tails suggesting that some separation of heavier white spirit components took place. The peak heights were about a quarter of these for the technical gasoline which gave generally more narrow and symmetrical peaks.

These findings do not support the suggested electron capture mechanism[27] for the negative FID response to CD and point to some other ionisation suppressing effect, probably a thermal or a dilution one.

An interesting conclusion can be drawn from these results, namely that the dichotomous process postulated in[22] to explain the FID response to CD is limited to CD molecules and takes place probably before their disintegration occurs. Otherwise, the ion forming process inhibition would not be restricted to CD molecules only and would affect also the concentration of ions formed from coeluting hydrocarbons with a more pronounced decrease of their response than was noted. Alternatively in connection with a possible preoxidation of CD in the FID flame to inactive species as suggested in ref.[25,27], this fact would also point to thermal or dilution effects rather thant to the electron capture[25]. Still another possible explanation for the anomalous FID response to CD including a kinetic or a thermodynamic control of the formation from CD of species inhibiting ion forming processes seems less likely when large differences in concentrations of coeluting CD and hydrocarbons are taken into consideration. In other case a much greater suppression of the FID response to hydrocarbons than was found should be observed.

FID Response Linearity

As shown in Table II, responses which can be reasonably well approximated by a straight calibration line were obtained for the studied concentration range in all cases. Only slight variations in otherwise high values of the coefficient of correlation r_{xy} took place in day to day work. There were also slight variations in slope and intercept values suggesting the desirability of performing the calibration procedure with each batch of samples or on a daily basis for most precise results.

Statistically significant positive intercepts for regression lines obtained during the work point to some degree of additivity between CD and hydrocarbons peaks but in all cases they are smaller than corresponding peak height ratios for CD itself. The ionisation suppression effect of CD is probably responsible for the negative intercepts of regression lines obtained for white spirit using instrument B. In some cases the CD ionization suppression effect counteracting the FID response to CD resulted in zero intercepts.

When plotted, the dependence of the peak height ratios on injected volumes are similar as reported previously[33-35] suggesting thus the presence of the volume effect. Although plot curvatures for technical gasoline and white spirit are of opposite direction, this is consistent with similar plots displaying often minima which are presented for greater concentration ranges in[34].

Results of Desorption Efficiency Determinations

Results given in Table III show that a relatively good reproducibility was achieved for both technical gasoline and white spirit as well as for Fomastatic NDF sampling and analysis. Differences in values calculated using multipoint and single point approaches also show that the CD response contributes to final results. These differences are more pronounced for the technical gasoline. The effect of varying analyte load is given in Table IV where differences in calculation approaches are even more marked. Here for the technical gasoline, the single point approach yielded slightly more consistent DE values and similar results were obtained also for Fomastatic NDF. For the white spirit, the consistency of DE values was slightly better for the multipoint approach, the contribution from the CD response being more pronounced and thus the correction achieved through the intercept value subtraction gave better results.

Significant as they may seem, these differences are relatively small compared to often large sampling variances. Therefore, in connection with the rule[36,37] predicting a negligible improvement in the overall precision of analysis by lowering analytical uncertainty when it has already fallen under $1/3$ of the sampling uncertainty, the analytical precision obtained for the proposed method, after the correction for DE, is considered adequate.

Field Test Results

As shown in Fig. 3, both IR spectroscopy and GC yielded comparable results for paired samples when the DE value of 107% was used for the GC method. When all paired values were pooled $(n = 16)$, the correlation coefficient value r_{xy} highly exceeded the critical value even for $\alpha = 0.001$. The regression line intercept value b_0 did not differ significantly from zero $(\alpha = 0.05)$ suggesting thus that the GC method results are not biased. The difference between the regression line slope value b_1 and unity was also found to be statistically insignificant $(\alpha = 0.05)$ pointing to a good agreement between the control (IR) and tested (GC) methods.

The smaller scatter around the regression line of the points representing control values obtained by measuring IR transmittances of CD eluates analysed simultaneously by GC is caused by the absence of the sampling variance contribution to the overall variance of paired results. When a separate regression line was calculated for this subset of values $(n = 5)$, results followed closely the pattern obtained for the whole set of values, confirming thus previous conclusions.

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