USE OF THE METHODS OF SOLID PHASE FUNCTIONAL, GROUP ANALYSIS FOR THE CHARACTERIZATION OF ORGANIC FUNCTIONALITIES IN BRAZILIAN OIL SHALES[1]

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ABSTRACT

The determination of the organic functionalities of bitumens and kerogens in oil shales has been approached by using chemical methods in which one solid phase is always involved. The Solid Phase Approach to the analysis of complex mixtures comprises three main methods: 1. **The Solid Phase Functional Group Analysis Method**: used for the analysis (qualitative and quantitative) of soluble compounds (bitumens and tars); is based on colored products formed by chromogenic reactions of specific functional group reagents bound to the surface of a solid matrix, with the corresponding groups of the substrate. 2. **The Solid Phase Functional Group Extraction Method**: used for separating a complex misture into fractions containing a specific functional group. It is based on the reaction (reversible) of a solid phase functional group reagent with the corresponding compounds in a substrate. 3. **The Solid Phase Functional Group Marker Method** used for the functional analysis (qualitative and quantitative) of solid substrates (kerogen), is based on the amount of a marker incorporated into the solid phase by means of reaction with marked specific functional reagents (soluble).

Oil shales, as they are known today, can be defined as "an intimate and apparently disorganized mixture of substances, amongst the most complex known (both the substances and the mixtures). They are, on one hand, made from an organic matter phase originating from the substance of different living beings, many of them fossils. If the (molecular) chemical composition of a living being is, in itself, a problem of extreme complexity, what word should be used for oil shales, that are a mixture of remains of many (how many?) different species, genus, families and even kingdoms – plants and animals (many more plants than animals), that over millions of years are being submitted to processes of transformation, practically unknown, following pathways determined by varying environmental conditions of temperature, pressure, catalysis etc. On the other hand, the inorganic phase of oil shales is mainly constituted by clays (clays constitute a very complex class of inorganic matter) and carbonates, containing sometimes pyrite and other minerals, all intimately mixed with the organic phase, probably participating in, or even promoting the transformations of the organic matter"[1].

This definition of oil shales shows the extreme complexity the microscopic (chemical) structure of these materials present and the problem they bring to the geochemist searching for a "significative structure" for them.

In order to reach a chemical structure of oil shales, four distinct levels of chemical information are needed[2];

1. The **elementary composition** – This is the simplest level and tells only which chemical elements (major and minor constituents) are present in oil shales and their proportion. This kind of knowledge is available for the majority of the oil shales known.
2. The **chemical functionalities**, that is, the connective arrangements of elements in small groups giving rise to characteristic "functions" (chemical or physical). They constitute the Functional Groups. Information in the literature is scarce about methods and results for determining functional groups directly on oil shales (bitumens and kerogens). Nakayama[3] prepared a comprehensive review of the methods used and results obtained for the chemical functionalities of the various oil shales in the world.
3. The **molecular composition**: A further degree of connectivities among chemical elements define molecules (minerals are to be considered as molecules). Characterization of molecules present in oil shales is one of the most active areas of research in the chemistry of oil shales nowadays. The advent of the capillary GC/MS/computing systems has allowed the characterization of hundreds of molecules of varying complexity from simple linear saturated hydrocarbons to highly complex substituted polyterpanoid skeletons. Indeed, this is the first step toward determining the geochemistry (the study of the natural transformations) of oil shales.

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The ultimate structure will be reached with the knowledge of

4. The **geochemical arrangement** of the atoms – or more precisely of functional groups and molecules – in the rock, i.e., the relative position of the chemical species in the three dimensional network of the solid phase. Information at this level is practically non-existent for oil shales. This situation will certainly be changed as further knowledge of sitons[4] will be needed to explain the natural chemical transformations in oil shales.

This paper is directed at presenting and discussing a strategy for determining chemical functionalities in oil shales based on the use of solid-phase reagents and discussing some results generated.

THE SOLID PHASE APPROACH TO OIL SHALE ANALYSIS

In a first approximation, oil shales can be considered to be formed of:

1. an organic phase soluble in organic solvents: the (natural) bitumen;
2. a second organic phase, insoluble in organic solvents: the kerogen;
3. a mineral aggregate, composed mainly by clays and carbonates and other minerals in minor amounts.

These phases coexist in an extremely high degree of intimacy in oil shales.

The standard procedure to separate them is to use solvent extraction of bitumens followed by the digestion of the inorganic matrix of the residue leaving the kerogen unattacked.

Shale oils are a class of materials derived from oil shales by pyrolysis (retorting). Shale oils – sometimes also referred to in the literature as shale tars, pyrobitumens or even bitumens – represent the way oil shales have been mostly used by society. Although use has been restricted mainly to fuel applications the knowledge of the chemical constitution of shale oils is becoming increasingly important.

These oils contain the cracked organic matter of kerogen and bitumen. The cracking process changes the original chemical structure through a considerable reduction in the size of the molecules, resulting in components that are volatile (can be distilled) and soluble in organic solvents. There is also a considerable increase in the double-bond character (unsaturation), and production of aromatics. The relative amount of the various classes of compounds of shale oil is dependent on the nature of the oil shalc but, mostly, on the pyrolysis temperature.

Bitumens are very thick high boiling oils, very dark in colour, composed of a myriad of chemical constituents. Standard procedures for their analysis involves fractionation by solubility (asphaltene precipitation in the presence of an excess of a low molecular weight alkane such as pentane) followed by chromatography (column or thin layer) of the maltene (pentane-soluble fraction).

Hydricarbons are then separated and further fractionated into aliphatic, naphthenics and aromatics; capillary gas chromatography/mass spectrometry allows the ultimate characterization of the individual molecules. Most of work reported in the literature refering to the components of oil shale bitumens deals with hydrocarbons. Carboxylic acids are a class of compounds easy to isolate by means of alkali extraction. The recovered acids are esterified (methyl esters) and characterized by CG/MS.

In the Irati oil shale (natural) bitumen, hydrocarbons form about 1/3 of the total bitumen weight. Although the content of the other elements (oxygen, nitrogen and sulfur) is small, it is possible to see that they are present in the remaining 2/3 of the bitumen, as functional groups attached to the various hydrocarbon chains. Carboxylic acids represent 2–3% of the weight of this bitumen.

The strategy chosen at "Projeto Xistoquímica" for the analysis of the non-hydrocarbon-non-carboxylic acid part of the bitumen (also in tars), was that of fractionating the mixture into isofunctional sets of substances, i.e., groups of substances containing a functional group common to the various constituents of the set[2]. In order to accomplish this, a method, based on Solid Phase Reagents, was developed.

The use of this method requires, first, the characterization of the functional groups present in the mixture. Any method chosen to perform this task in bitumens (and tars) should take into account that:

1. The functional groups are generally present in very low concentration ($< 0,1\%$).
2. The number of components of any functional class (isofunctional set) if always very high (> 100).
3. Bitumens are extremely dark, viscous and high boiling.

Functional Analysis: A chemical approach based on Feigl's Tests (Spot Tests)[5] was initially considered for characterization of the functional groups in bitumens and tars, since these tests are very sensitive and can be made specific for the various functional groups. The great majority of these tests are chromogenic (producing chromophores with very high absortivities in the visible), leading to appearance or change of color. The characteristics of bitumens described above (very dark color and very low concentration of functional groups) practically discard the possibility of using the Feigl Tests for this purpose. Nevertheless, Costa Neto *et al.*,[6] were able to perform a set of 63 of these tests on Brazilian oil shales, using small adaptations in each case. Aldehydes and ketones were also characterized directly in the Irati[7], Vale do Paraíba and Marau[8] oil shale bitumens by using Spot Tests.

Feigl Tests can be made feasible for detecting organic functional groups in bitumens and tars if the specific functional reagent is (chemically) bound to a solid matrix.

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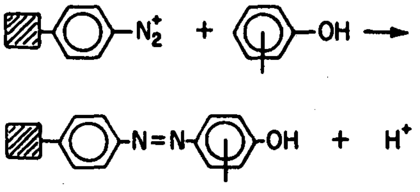
[2] Further fractionations could lead to homogunctional sets, where *all* the functional groups are common to all the components of the set.

For instance, a phenyl diazonium salt bound to the surface of polystyrene is able to collect on this surface phenols and aromatic amines present in the bitumens: as the hydroxy or aminoazo compounds are strongly colored, the surface of the polystyrene becomes stained when these groups are present in the substrate:



The literature contains examples[9] of uses for this type of compounds and reactions but they are restricted mainly to the area of ion exchange resins and chelating reagents for metals. More recently Gosnell & Mottola[10] used p-nitrophenylhydrazine to determine the amount of glutaraldehyde bonded to an aminosilylated silica surface (the bonded hydrazine was released from the solid surface and measured photometrically in solution). Nevetheless, it seems that these reagents, as a class – the Solid Phase Functional Reagents (SPR) – have not yet been used, systematically, as a tool for the functional analysis of complex materials.

Although they represent an extension of Feigl's concepts to organic functional analysis, they offer new features, that are, indeed, decisive as a method to characterize functional groups in bitumens and other complex materials:

1. They present a concentration effect, since the functional reagent can be restricted to a small area of a polymeric film. This is of particular importance in the analysis of bitumens since their "diluted" functional groups can be collected into the small surface giving rise to a marked increase in concentration and consequently allowing for better conditions for characterization.
2. Only the specific substrates will be bound to the polymeric matrix. After the "fixation reaction" is completed, the solid phase is taken out for the bitumen and washed free of all other contaminants. In this way it is possible to obtain in the solid matrix the chromogenic group, specific for the functional group sought, free from other colored molecules[3].

If a small thin disc of a transparent polymer is used as support, a visible spectra of the product can be taken and interpreted in terms of the nature of the constituents (through its λ_{max} value) and amounts (through the absorbance at a given λ). This procedure is presently being developed to be used as a quantitative method to determine the amount of a given class of compounds present in bitumens (also in tars).

3. The method can be used for very small amount of samples.

At present, most of the work on this method has been restricted to the use of phenyl diazonium chloride bound to a polystyrene matrix[11] for the characterization of phenols in shale oil.

SEPARATION OF ISOFUNCTIONAL SETS OF MOLECULES: The knowledge of the functional groups present in bitumens provides an important class of information regarding these materials, but a greater knowledge about the chemical compounds to which they belong is necessary.

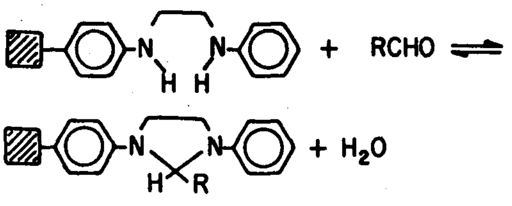
A solid phase approach can also be used in this step: to fractionate the mixture into functional classes of compounds (isofunctional sets) – say aldehydes, primary amines, mercaptans etc. – by means of the Solid Phase Extraction Method[7,12,13]

Similar to the solid phase reagents used for functional analysis the reagents used for solid phase extraction contain a functional group reagent bound to a solid matrix. Nevertheless, the reagents and reactions used in either situation are quite different. Table I gives a comparative view of the main characteristics of the reagents and reactions used in these cases.

The above mentioned reaction used for detecting phenols by means of a polymer-bonded diazonium salt[4] should be avoided for a solid phase extraction objective, since the recovery of the phenol from the azo compound formed is not a straighforwad procedure. In this case it would be better to use a s-phenyl isocyanate.

The solid phase extraction method involves the following main steps:

1. A given class of compounds (say aldehydes, for examples) is "fished" from the bitumen (the procedure is valid for any other complex mixture) by means of a specific "bait" (the functional reagent; in the case of aldehydes it may be a diphenylethylene-diamine group) connected to the "fishing rod" (the polymeric support; polystyrene can be used in this case). This constitutes the fixation step.



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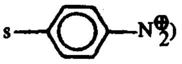
[4] The notation s-functional group reagent (e.g. ) will be used to denote the solid phase-bonded functional group reagent.

[3] A variation of this approach could be used to characterize the colored molecules of bitumens. For this purpose a specific functional reagent is attached to the polymeric matrix, but the reaction with the substrate should not lead to a chromophoric group, that is, no color should be produced due to the bond formed. In this way, only the colored molecules containing that particular group would confer color to the solid phase reagent.

Table I. Characteristics of the reagents and reactions used in the functional group analysis and solid phase extraction.

Functional Groups Analysis	**Solid Phase Extraction**
Reactions should lead to appearance of color (chromogenic reactions).	Reactions do not need to be chromogenic.
Reactions do not need to (should not) be reversible.	Reactions must be reversible or, at least, the product must easily restose the initial substrate or a very close relative.
Original molecular structure (hydrocarbon chains) do not need to be maintained. In this way "strong" reacting media like concentrated acids may be used.	Original molecular structure of the compounds must be maintained. So, reaction conditions must be mild.
In some of the characterization reactions the mechanisms are not well known and in some cases, not even the structure of the product.	All mechanisms involving the reactions of fixation and restoration must be well known, as well as the structure of the compound formed.
Reactions yields do not need to be high (low yields will of course reduce the identification limits).	Reaction yields must be the highest possible (extraction should exceed 90%).
Reactions are, generally fast (1-5 minutes) and the experimental procedures are about the same as for Feigl Tests (very simple).	(Reactions may be slow (hours). Experimental procedures are similar to the ones used in small scale synthesis, using operations like refluxing, filtering etc.
Reagents can be restricted to a small area in the surface of the polymer-support since the detection methods to be further used are very sensitive.	A high concentration of functional group reagent is needed, since it is used primarily for "preparative" goals.
Its use is restricted to characterization of functional groups in the mixture.	It is a step towards the characterization of the individual molecules.

2. The solid phase now containing the fixed compound is separated from the bitumen and thoroughly washed with an appropriate solvent in order to get rid of all unreacted components of the bitumen (the separation step).

3. The fixed compounds are liberated from the solid phase (generally by means of hydrolysis) to form an isofunctional set of compounds (the recovery step) (in the above mentioned example all compounds will have an aldehyde group).

4. The isofunctional set is further separated by chromatography and analysed by mass spectrometry in order to characterize the individual compounds.

Fundamental work regarding Solid Phase Reagents has bech extensively conducted by Pinto[13] with standard compounds and different types of SPR. It was shown that:

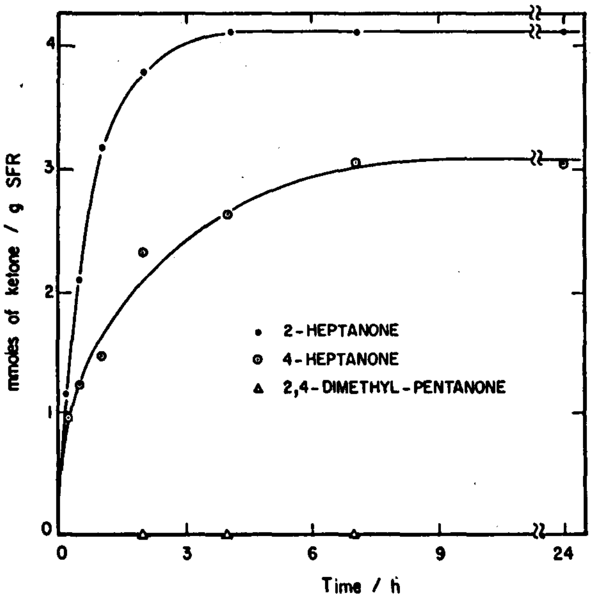


Figure 1. Steric effect on the fixation rates of C_7-ketones (2-heptanone, 4-heptanone and 2,4-dimethyl-pentanone) by s-carboxyl hydrazide[13]. Excess of ketone was used.

1. They may present **steric discrimination**. The present generation of SPR, in which the reacting groups are directly linked to the surface of the polymer seems to discriminate compounds in which the functional group is near bulky substituents. Pinto[13] showed (Fig. 1) how the rate and yield of fixation of C_7 ketones by s-carboxy hydrazide varies according to the substituents near the functional group (2-heptanone, 4-heptanone and 2,4-dimethyl pentanone). A dramatic difference in behaviour can be observed: the methyl ketone is quantitatively extracted, but the diisopropyl is not extracted at all. The di-n-propyl is fixed in lower yields and more slowly than the methyl one. With this SPR it was also shown that 2-heptanone and 2-tridecanone show different (Fig. 2) rates of fixation (the smaller chain fixes faster) but the extraction yields are about the same.

2. **Ageing** may be a problem with some SPR. The s-carbonyl hydrazide showed a remarkable decrease in activity when stored in contact with air. This decrease was not so drastic if it was kept sealed under an inert atmosphere (Fig. 3).

3. The **solvent** used has a pronounced effect on the kinetics and yields of fixation. Figure 4 shows the effect of metha-

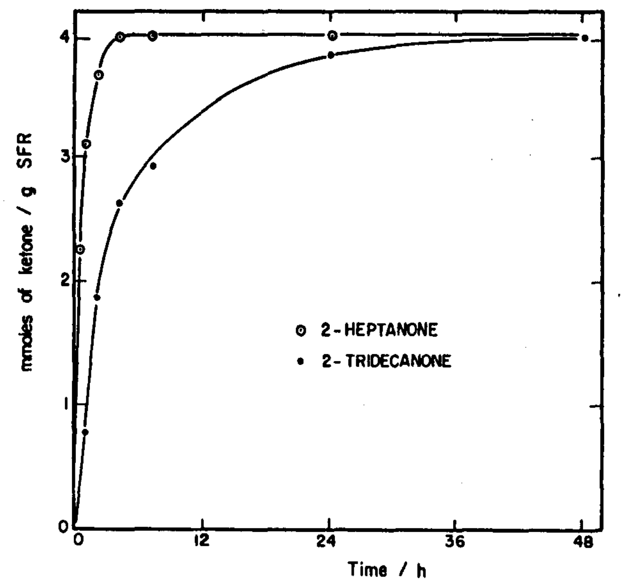


Figure 2. Rates of fixation of 2-heptanone and 2-tridecanone by s-carboxyl hydrazide[13]. Excess of ketone was used.

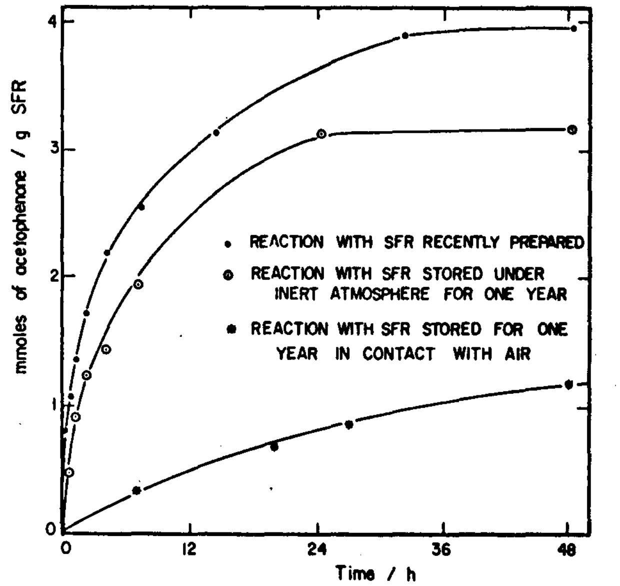


Figure 3. Ageing effect on s-carboxyl hydrazide (acetophenome used as substrate)[13]. Excess of acetophenone was used.

nol, methanol-benzene (1:1) and methanol-tetrahydrofuran (THF) (1:4) upon the fixation of acetophenone by s-SO_2NHNH_2. In pure THF or in pyridine no fixation was observed.

4. The **nature of substituents** influences the yields and rates of fixation; Figure 5 shows the distinct behaviour in fixation of 2-heptanone, 2-tridecanone and acetophenone by the s-sulphonyl hydrazide reagent (compare with Fig. 2 in which the final yield of fixation is the same for 2-heptanone and 2-tridecanone).

The solid phase extraction method has been used to isolate aldehydes, ketones, alcohols and amines from Brazilian oil shales[7,8,13].

Kerogen is defined as the insoluble organic phase of oil shales. This insolubility adds a new difficulty to the analysis of kerogens, relative to those mentioned for bitumens. For all practical means, kerogen can be considered a macromolecular; amorphous, solid phase.

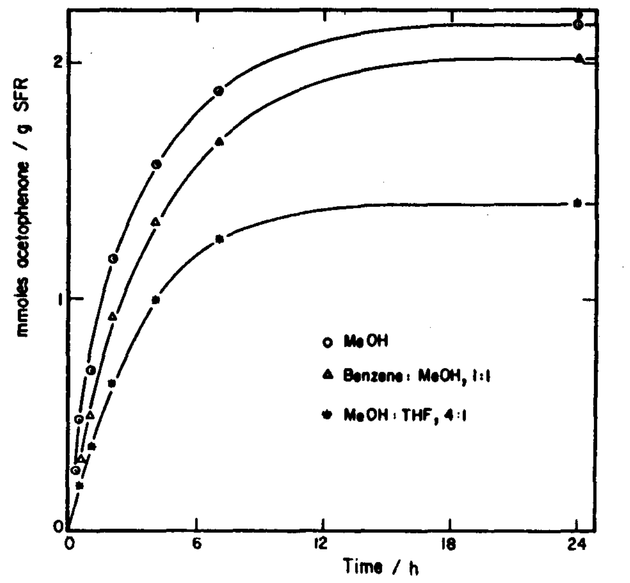


Figura 4. Solvent effect on fixation rates of acetophenone on s-sulphonyl hydrazide[13]. Excess of acetophenone was used.

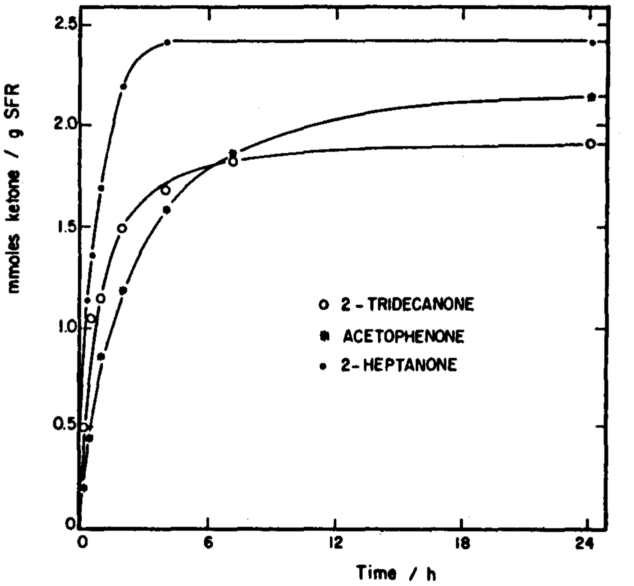


Figure 5. Effect of substituents on fixation rate of ketones (2-tridecanone, acetophenone, 2-heptanone) by s-sulphonyl hydrazide[13]. Excess of ketone was used.

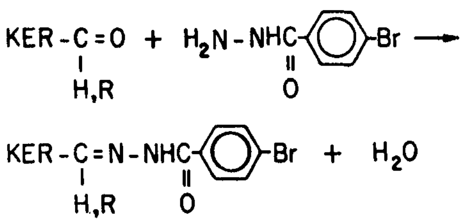
Functional groups play an important role in the chemistry of kerogen since they represent the reactive spots in the molecules.

In oil shale chemistry knowledge of their nature is important as a first step towards understanding the natural transformations of kerogen (maturation).

In order to characterize and quantify the functional groups present in kerogen, a third approach using a solid phase was developed – now the solid phase being the kerogen itself: it constitutes the Functional Marker Method.

FUNCTIONAL MARKER METHOD: In this method, kerogen is made to react with a (soluble) functional reagent containing a **marker**. This marker may be any kind of a particular characteristic that can be easily identified (or better yet quantitatively determined). It can be a radioactive tracer, a fluorescent moiety, or an element not present in the solid phase being studied. Halogens have been mostly used as markers in the study of kerogens. Table II gives a list of functional reagents used to determine functional groups in Brazilian oil shales[12].

For the characterization of carbonyl compounds (aldehydes and ketones) p-bromobenzhydrazide has been used:



The amount of bromine (the marker) incorporated in kerogen is a measure of the amount of the carbonyl groups it contains.

The method is simple to apply but two points must be kept in mind by those using it:

1. Althought the yields are high with the chosen reagents, one must be sure that all "available" centers have reacted. This can be accomplished repeating, successively, the reaction of incorporation of the marker, intercalated with determinations of the amount of marker incorporated: two successive equal results gives in indication of saturation.

One must bear in mind, too, that kerogen has also a highly complex "physical" structure, thus part of the functional groups (of a same type) may be "hidden" and consequently not "available" for reaction with the marked functional reagent. The measured amount of functional groups should be taken, only, as the **minimum**, even though saturation has been reached.

2. In order that any result be of any significance one must be sure that all non-reacted reagent has been washed away from kerogen. This is not a trivial operation, since the complexity of kerogen may permit it to keep some adsorbed or dissolved reagent in it. Again, a series of successive extractions of the reagent from kerogen, with a solvent in which the reagent is highly soluble, must be conducted and the presence of tracer must be evaluated in each extract. Only when no more tracer can be detected, may the extraction process be discontinued.

Table II. Functional reagents used in the functional marker method[13]

Functional Group	Functional Reagents
AMINE	
primary	p-chlorobenzaldehyde
primary aromatic through diazonium salt of kerogen	p-chloroaniline o-chlorophenol
AMINE/HYDROXYL	
primary and secondary amines, alcohols	p-bromobenzoyl chloride
phenols, aromatic amines	p-chlorobenzenediazonium chloride
CARBONYL	
aldehydes	p-chloroaniline N,N' (p-bromophenyl) ethylenediamine
aldehydes and ketones	p-bromobenzhydrazide
CARBOXYL	p-bromophenacyl bromide
HYDROCARBON	
allylic/benzilic	N-bromosuccinimide
unsaturation	bromine (water)
"para" position in phenols	2,6-dibromo-N-chloroquinoneimine

EXPERIMENTAL PROCEDURES: Procedures applied to oil shales are peculiar to each method described and, within each method, to each functional group sought. So far there are not many results in the literature regarding these methods. The available references are grouped in Table III.

Table III. References to experimental procedures dealing with solid phase functional analysis, solid phase extraction and functional marker method applied to oil shales

Method	References
Solid Phase Functional Analysis	11
Solid Phase Extraction	7,8,12,13
Functional Marker Method	3,12,15

USES OF THE SOLID PHASE APPROACH TO ANALYSIS OF OIL SHALES

The Solid Phase Functional Analysis. The solid phase functional analysis of oil shales has been practically restricted to the detection of phenols in the Irati shale oil by Castro[11], who used a polystyrene matrix with diazonium groups attached to it (the dried strips are stable for weeks).

After reaction with shale oil the polystyrene containing the phenyl diazonium reagent, becomes yellow. Its visible (700-400 nm) absorption spectrum is shown in Figure 6. In the same figure, a set of spectra obtained in similar conditions for known phenols and naphthols is also presented.

The Solid Phase Extraction. The main functional classes of compounds studied by the solid phase extraction method were aldehydes and ketones.

Aldehydes were extracted from bitumens by means of the reagent s-N, N'-diphenylethylenediamine already mentioned.

They are recovered from the resin by acid hydrolysis and further separated and characterized by GC/MS. The series of aldehydes isolated from Irati oil shale by means

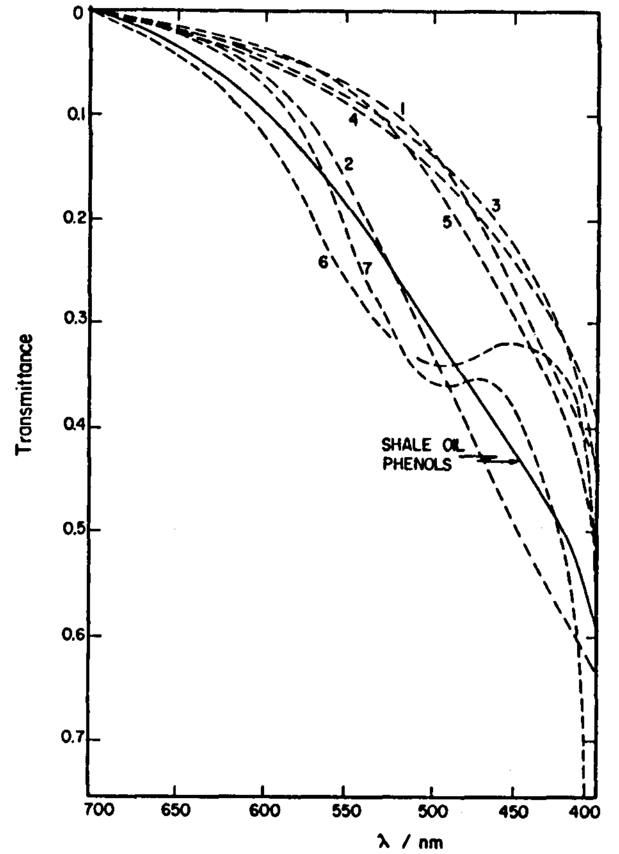


Figure 6. Visible absorption spectra of solid phase binded shale oil phenols and reference compounds. 1. Phenol; 2. Resorcinol; 3. Salyciclyc Acid; 4. m-Cresol; 5. p-Cresol; 6. 1-Naphtol; 7. 2-Naphtol[13]

of the Solid Phase Extraction are described in Table IV.

The use of this method permitted the separation of the homologous series of linear aldehydes (C_{12}-C_{33}) from the Vale do Paraiba (São Paulo, Brasil) oil shale[8].

Aldehydes represent a class of compounds of particular importance to organic geochemistry. Two main situations may account for their presence in oil shales:

TABLE IV. Series of aldehydes and ketones isolated from Irati oil shale

Aldehydes	Ketones
alkyl benzaldehydes	alkyl acetophenones
alkyl phenylacetaldehydes	alkyl 1-indanones
alkyl naphtaldehydes (methyl and dimethyl)	alkyl acetonaphthones (methyl and dimethyl)

1. They are well known components of living plants; so, their presence in sediments may be taken as a remnant of the materia-prima. But, considering that the aldehydes found in the Vale do Paraiba oil shale are quite different from those found in Irati, and knowing that the aldehyde group is rather reactive, it should be asked what mechanisms led to the degradation of the organic matter in oil shales while leaving the aldehyde group undisturbed?
2. They were formed in the diagenesis process: in this case which mechanisms would be responsible for its formation? Could it be a microbiological alpha-oxidation of hydrocarbons as suggested by Chicarelli[8] for the Vale do Paraiba oil shale? Of course it can not be any chemical oxidative route since the medium is highly reductive. No direct reduction of carboxylic acids to aldehydes has been demonstrated to the present (Vernemismer *et al.*,[14] presented evidences for geochemical reduction of carboxylic acids to the respective hydrocarbon moiety).

This is not the place to try to answer these questions but only to show that they could be raised based on the available information regarding the presence of aldehydes (as a group) in various Brazilian oil shales and that this information was available due to the Solid Phase Extraction Method.

Ketones were isolated from Irati oil shale by means of s-carbonyl hydrazide:

$$\text{s}-\underset{\text{O}}{\overset{}{\text{C}}}-\text{NHNH}_2 + \text{O}{=}\text{CR}_1\text{R}_2 \underset{\text{H}^{\oplus}}{\rightleftharpoons} \text{s}-\underset{\text{O}}{\text{C}}-\text{NH}-\text{N}=\text{CR}_1\text{R}_2 + \text{H}_2\text{O}$$

Table IV shows the ketones isolated from Irati oil shale. 6,4,10,14-trimethylpentadecan-2-one is, by far, the major ketonic component of the Maraú (Bahia, Brazil) oil shale (Fig. 7).

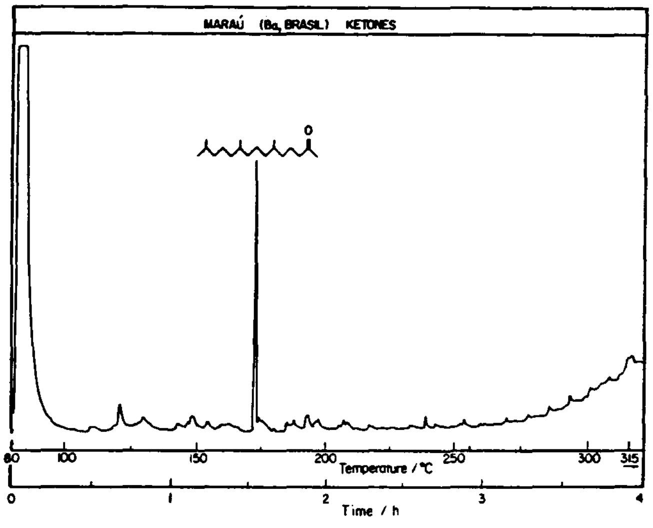


Figure 7. Ketones from Maraú (Bahia, Brasil) oil shale bitumen.

Cyclic ketones (hopanones etc.) seem to be discriminated against by the present generation of the Solid Phase Extraction Reagents. Very little of these compounds is extracted by the s-hydrazide. Developments are in progress to overcome these difficulties.

The Functional Marker Method: This method has been used to measure the content of functional groups in kerogens of Brazilian oil shales.

The absolute knowledge of the functional group content is, undoubtedly, an important set of information about kerogens. It is possible to know for instance, the fraction of the total amount of a given element, present as a specific functional group (e.g. how much of the total nitrogen of a kerogen is present as primary amine or how much of the

TABLE V. % Of total element present as the functional group in Brazilian oil shales kerogens

Oil Shale	% Of Total Carbon AS		% Of Total Nitrogen as Primary Amine[3]
	Carboxylic Acid[1]	Carbonyl Group[2] (Aldehyde + Ketone)	
Irati	1,11	0,25	5,0
Vale do Paraíba	1,93	1,18	3,3
Maraú	1,05	0,72	3,3

[1] determined with p-bromophenacyl bromide

[2] determined with p-bromobenzhydrazide;

[3] determined with p-chlorobenzaldehyde.

total carbon is involved in aromatics containing a phenolic group etc.).

Table V give such results[12] for some Brazilian oil shales. As can be seen from Table V the nitrogen present as primary amine in the Irati oil shale kerogen, e.g., represents 5,0% of the total nitrogen. The balance can be attributed to the following main causes:

1. The existence of functional groups different from those determined. This is the most obvious conclusion. The search for new groups should be then conducted. Nevertheless, one should also consider that
2. the analysed functional groups were not totally available to the reagent – this is a real possibility with regard to the groups present inside kerogen "particles". It should also be considered that
3. although the method has been conducted to saturation of kerogen by the reagent, the equilibrium constant may not be large and the group content is being undermeasured.

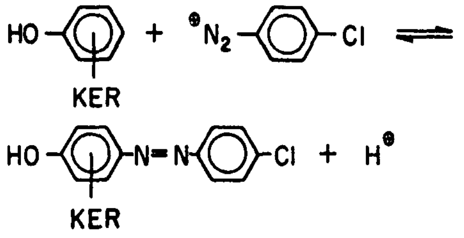
TABLE VI. Relevant points for using the solid phase approach to the analysis of oil shales

Method	Objectives	Advantages	Present day Problems
Solid Phase Functional Analysis	Characterization and determination of organic functional groups in bitumens and tars	Can be made specific for a given functional group. Allows for determining functional groups in low concentrations (high sensitivity). Can be used for both qualitative and quantitative determinations. Functional groups can be characterized (or determined) in strongly, colored solutions or suspensions. Experimental procedures are very simple.	Very limited number of reagents available. The polymers used as solid phase support presents problems in respect absorption of oils. Quantitative procedures incipient.
Solid Phase Extraction	Fractionation of a complex mixture (bitumens and tars) in isofunctional sets of molecules	Complex mixtures can be separated into fractions, each containing the same functional group. Can be used with small amounts of substrate (as a micro method) or in large scale applications. It is non-destructive. Compounds are recovered. Experimental procedures are very simple.	Limited number of reagents available. Steric discrimination observed with cyclic ketones. Very little is known concerning the physical organic chemistry of both fixation and liberation processes.
Functional Marker	Characterization, determination and localization (?) of functional groups in kerogens	Allows for characterizing or determining specifically organic functional groups in solid substrates. It is a direct, absolute method. It can be used for small amounts of sample. With appropriate markers localization of functional group clusters in the solid phase surface can be considered. Experimental procedures are very simple.	Sample is consumed in tracer determination. It is difficult to ascertain that all groups have been reached by the reagent (inner inaccessible groups). Very little is know about the physical organic chemistry of the reactions involved.

At the present stage it can be said that much work is still needed to use the reagents indicated by Costa Neto *et al.*,[12] and others and that the content of a given functional group in kerogen must be checked with more than one reagent in order that reagents and procedures will lead to results that can be accepted with confidence.

But, in any of the cases mentioned above, the Functional Marker Method indicates a clear line of investigations to be followed towards the knowledge of the organic functionalities in kerogens.

The Functional Marker Method was used to determine the degree of "phenolization" (aromatization with phenol formation) of kerogen in a stratigraphic column of the Irati Formation which has been (naturally) submitted to a localized heat source (due to a diabase intrusion)[15]. In other words, a correlation was sought between the stratigraphic functions for (paleo) temperature and phenol content. The p-chlorobenzene diazonium cloride was used as the functional marker for phenols.



The results indicated the existence of an inverse correlation (i.e., the point of highest temperature corresponded to the lowest phenol content (Figure8)). The geochemical implications of this correlation are discussed elsewhere[15]; here it is enough to say that the Functional Marker Method provided a simple and direct method for determining the phenol content in kerogen.

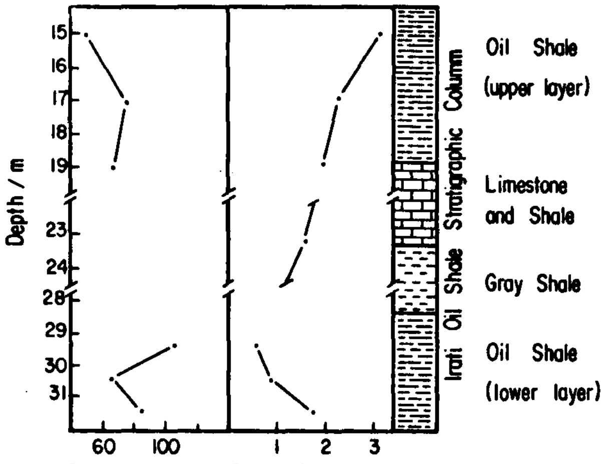


Figure 8. Correlation between the stratigraphic functions for paleotemperature and phenol content in kerogen determined by the Functional Marker Method, for the column CERI-1 from the Irati Formation[15]

In conclusion, it can bė said that the SOLID PHASE FUNCIONAL GROUP aproach to oil shale analysis is a group of methods for studying the chemical composition of oil shales having in common:

1. They are chemical methods involving the organic functionalities of the substrate (bitumens, kerogens and tars).
2. They involve reactions of "matching functionalities" i.e. specific reactions between two complementary organic funcional groups. One of them is present in the substrate (the searched functional group); the other is in the reagent (the specific funcional group reagent).
3. Always, in the matching pair of functionalities one of the funcional groups is bound to a solid phase; the other belongs to a soluble molecule. In the case of bitumens and tars – soluble substrates – the reagent was bound to a solid matrix (an organic polymer). In the case of kerogens – a solid substrate – the functional reagent was the soluble moiety.

Table VI presents a balance of advantages of using these methods and the present-day difficulties of applying them.

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