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PYROLYTIC EVALUATION OF STANIANCI LIGNITES FROM SOFIA COAL BASIN

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ABSTRACT

Atmosphere Pressure–Temperature Programmed Reduction (AP-TPR) coupled "off-line" with thermal desorption gas chromatography-mass spectrometry (TD-GC/MS) is used to evaluate qualitatively and quantitatively organic functionalities in Stanianci lignite from Sofia coal basin, Bulgaria. The total content of the identified compounds in pyrolysate is 22 mg g^{-1} C_{org}*. Alkyl benzenes (*C_6 *-* C_{10}*) referring to 44 rel. % dominate there. The low sample maturity reflects high abundance of phenols* C_6 *-* C_8 *(8.4 rel. %) and methoxy phenols (6.3 rel. %). The presence of 0.4 rel. % of sesquiterpenoids of predominantly cadalene skeleton, suggests gymnospermous flora contribution to the Stanianci coal-forming palaeomire. The arrangement of the four classes of organic compounds identified in pyrolysate, i.e. aliphatics, aromatics, O-containing compounds and S+N-containing compounds in a cluster diagram provides to outline some peculiarities of the fractional composition.*

All results obtained lead to the conclusion that AP-TPR combined with TD-GC/MS is a promising for analytical characterization of coal, for determination of the predominant vegetation in the coal-forming palaeomire and reconstruction of the palaeoenvironment.

Keywords: lignite, reductive pyrolysis, TD-GC/MS, coal sesquiterpenoids.

INTRODUCTION

Pyrolysis is a process which can be used to acquire detailed information for organic matter (OM) composition on a molecular level when it is combined with an appropriate detection system [1]. Atmosphere Pressure–Temperature Programmed Reduction (AP-TPR) technique coupled with a variety of detection systems has been developed and successfully applied to study sulphur functionalities in initial and biodesulphurized coals [2, 3]. The possibilities of AP-TPR technique can also be used for analytical characterization of different materials with geological provenance, i.e. lignite lithotypes, leonardite and coal humic acids [4 - 6].

The approach applied herein is focused on analyses of pyrolysis flue gases from Stanianci lignite using AP-TPR "off-line" TD-GC/MS and subsequent assignment of the registered components to the initial sample OM structural composition.

EXPERIMENTAL

Proximate analysis, i.e. ash (A), moisture (M), volatile matter (VM), fixed carbon (C_{fix}), was performed by TGA analysis using a DuPont Instruments 951 Thermogravimetric Analyzer and expressed in “as received base” [7]. Elemental composition, i.e. C, H, N, S, was determined with a Thermo Electron Flash EA1113 elemental analyzer.

Pyrolysis was carried out in the AP-TPR set-up described previously [5, 8]. Briefly, 40 mg of the demineralized sample and 20 mg of fumed silica were placed in a quartz reactor under a 100 ml/min flow of pure H_2. A linear temperature program of 5 °C min^{-1} from ambient temperature up to 950°C was applied. The technique was adapted to trap volatiles for subsequent GC-MS analysis as described in [4]. The outlet of the AP-TPR reactor was connected to a set of two ice-cooled tubes containing Tenax (Sigma-Aldrich), a porous polymer of 2,6-diphenyl-*p*-phenylene oxide, as adsorbent. The volatiles were additionally diluted by adding inert gas to the H_2 flow in ratio 5:1 (v/v) in order to prevent saturation of the adsorption tubes. Volatiles were trapped in two separated temperature ranges: 250^{o}C - 550^{o}C for the first tube and 550^{o}C - 950^{o}C for the second one.

The adsorption tubes were separately desorbed and analyzed by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS). The apparatus was used with He as carrier gas at 85 kPa under the following conditions: a) Unity thermal desorber (Marks): primary desorption for 20 min at 275ºC; cold trap at – 10ºC, heated at maximum heating rate up to 320ºC, hold time of 15 min; flow path temperature 200ºC; b) Trace GC Ultra-Gas chromatography (Thermo Instruments): capillary column 30m ZB 5-MS x 0.25 mm x 0.25 µm Phenomenex; temperature program - 3 min at 30ºC, heated at 8ºC/min to 100ºC, heated at 12ºC/min to 310ºC, hold time of 5 min; c) DSQ-Mass spectrometer (Thermo Instruments): EI spectra; Ionization energy - 70 eV; Scan range – *m/z* 33 - 480 in 0.4 s.

The homologous series and compounds were MS identified using single ion monitoring (SIM). The following diagnostic fragments were tracked: *m/z* 57 – *n*-alkanes; *m/z* 183 – regular isoprenoids; *m/z* 91, 105, 119 – alkyl benzenes; *m/z* 94, 108, 122 – phenols; *m/z* 84, 98, 134, 148 – thiophenes/benzothiophenes; *m/z* 128, 142 – naphthalenes; *m/z*154, 166 –biphenyl, fluorene; *m/z* 96, 118, 132, 146 - furanes/benzofuranes; *m/z* 94, *m/z* 126 – dimethyldi- and trisulphides; *m/z* 108, 124, 138 - methoxy phenols; *m/z* 79, 93, 107 – pyridines; *m/z* 103 – benzonitrile; *m/z* 198, 200, 202, 204 – sesquiterpenoids;

NIST library spectra were used for peak identification. The components were quantitatively determined using 3 µg deuterated thiophene, Th-d_4, as a standard.

RESULTS AND DISCUSSION

Stanianci lignite sample is characterized by the following proximate parameters, in wt. %, as received: M - 9.82; A - 3.65; V - 40.72; C_{fix} - 45.76; and elemental composition, in wt. %, on dry and ash free basis: C-62.48; H- 5.52; N - 1.86; S - 2.30; O^{diff}- 27.84;

TD-GC/MS chromatograms from 250^{o}C - 550^{o}C and 550^{o}C – 950^{o}C pyrolysates are shown in Figs. 1 and 2. Therein all peaks are identified and quantified but only the major ones are indicated. Concentrations of all compound classes detected in pyrolysates are listed in Table 1. The total sum of the identified compounds is 22 mg g^{-1} C_{org}.

The pyrograms in Figs. 1 and 2 demonstrate that a complex mixture of aliphatics, aromatics, and polar compounds is produced in the course of the reductive pyrolysis. These components might exist in the initial coal or, more likely, have been formed through secondary transformation.

Alkyl benzenes, i.e. C_6 - C_{10} are the main compounds in the pyrolysate in the 250^{o}C - 950^{o}C temperature range. They represent 44 rel. % of the volatile products (volatiles) released with the flue gases (Fig. 1 and Table 1). Their distribution is dominated by toluene in the low temperature region of 250^{o}C - 550^{o}C, while benzene predominates in the flue gases (Fig. 2) in the 550^{o}C - 950^{o}C temperature range. A similar pattern is recorded for “Maritza-East” lignite lithotypes [4]. Alkyl aromatics are generally considered as a product of humification of the primary plant materials and microbial metabolites.

Linear hydrocarbons, nC_6 - nC_{15}, i.e. *n*-alkenes/*n*-alkanes pair, are identified only in the first adsorption tube as the short-chain aliphatics dominate in the pyrogram (Fig. 1). Their presence can be attributed to the products of microbial activity, i.e. microbial lipids, or to fractions of long aliphatic chains attached to the aromatic structures of coals. Regular isoprenoids, i.e. *iso*-C_{14}, *iso*-C_{15} and *iso*-C_{16} are recognized as well.

Naphthalenes, biphenyls, acenaphthalenes, fluorenes and their alkylated analogues are detected in the higher temperature region (treating the second adsorption

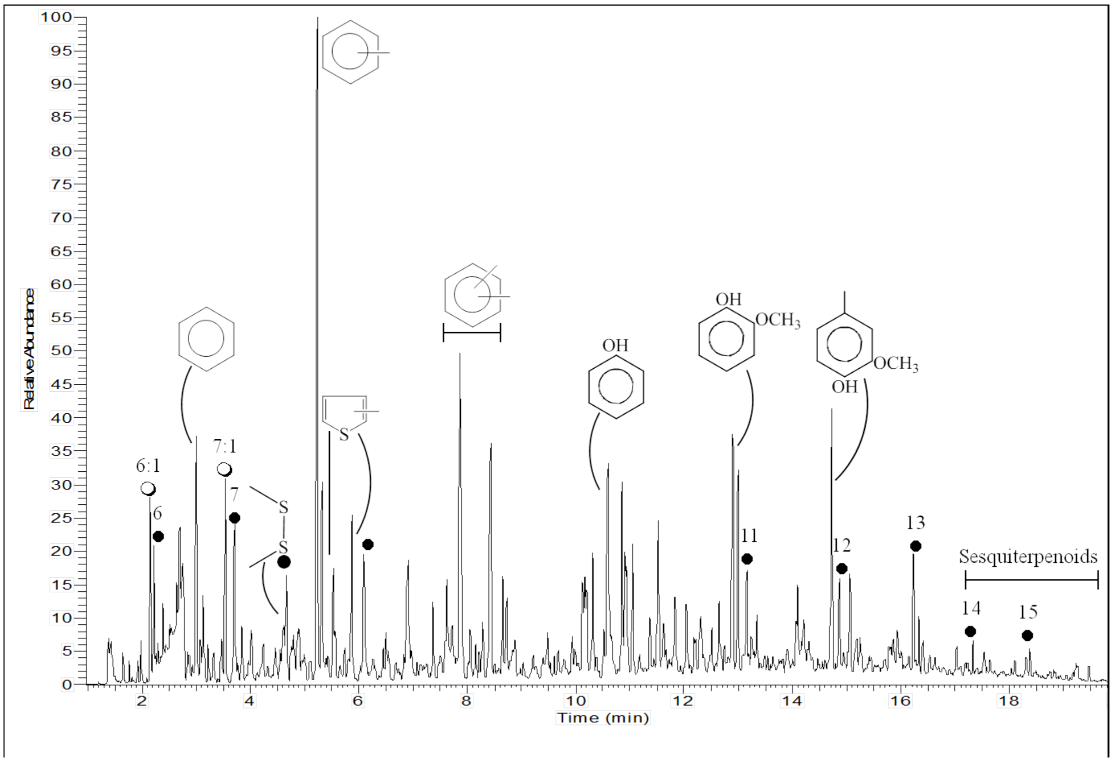

Fig. 1. Low temperature range 250 - 550°C pyrolysate composition of Stanianci lignite (Number - carbon atoms in *n*-alkene/*n*-alkane pair, ○ - *n*-alkene; ● - *n*-alkane).

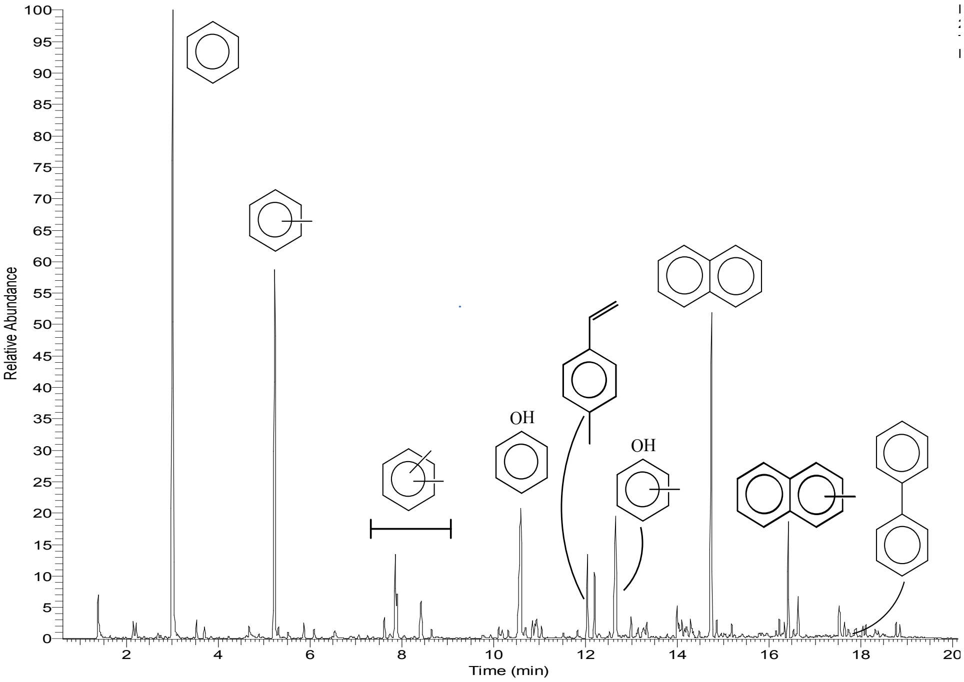

Fig. 2. High temperature range 550 - 950°C pyrolysate composition of Stanianci lignite.

Table 1. Compounds determined in reductive pyrolysate of Stanianci lignites.

No	Compounds	Content	
		μg g^{-1} Corg	%
1	*n*-Alkenes/*n*-Alkanes, i.e. nC_6-nC_{15}	4 769.7	21.7
2	Alkylbenzenes, i.e. C_6-C_{10}	9 674.0	44.0
3	Furanes/Benzofuranes/Dibenzofuranes	220.4	1.0
4	Phenols, i.e. $C_6 \div C_8$	1 858.2	8.4
5	Methoxy phenols	1 386.6	6.3
6	Naphthalenes/Biphenyls/Fluorenes	1 788.0	8.1
7	Dimethyl di-/trisulphides	578.1	2.6
8	Thiophenes/Benzothiophenes	1 534.9	7.0
9	Nitrogen containing compounds	104.3	0.5
10	Sesquiterpenoids	92.7	0.4
	Total	22 006.9	100

tube). Abundance of polycyclic aromatic compounds of a higher degree of condensation cannot be expected taking into consideration the parent coal immaturity. Mono- and diaromatic structures, i.e. alkyl benzenes and alkyl naphthalenes, are accompanied by a considerable portion of their sulphur analogues, i.e. thiophenes/ benzothiophenes (7 rel. %). Aliphatic S-containing compounds, i.e. dimethyl di- and trisulphides (2.6 rel. %) are identified as well.

The alkylated aromatic compounds are gradually replaced with temperature increase by phenolic structures, among which vanillyl phenols, i.e. 2-methoxy and methyl-2-methoxy phenols of 1386 μg g^{-1} C_{org} or 6.3 rel. % (Table 1) dominate. Methoxy phenols are indicative for the presence of residues from lignin in low rank coals. The high content of phenol and its alkylated homologues is a clue for a coalification process taking place through demethoxylation and subsequent phenolic structures rearrangement with aromatic structures cyclization.

The following sesquiterpenoids are identified in the lower temperature pyrolysate: dihydrocurcumene, cedrane, cuparene, cadinatrienes and cadalene (Fig. 3). All of them indicate the gymnospermous flora contribution to the coal-forming palaeomire as they are typical coal biomarkers comprising resins and essential oils of higher plants [9]. In combination with diterpenoids they serve to tag plant resins in the geological record and connect them with certain classes of plant input. Only cuparene among the sesquiterpenoids listed above is a specific chemosystematic marker for palaeovegetation. Its derivatives are found only in modern species of Cupressaceae/Taxodiaceae. Compounds of a cadalene skeleton are common constituents of resins and ambers, and of petroleum of a terrigenous input [9].A similar set of sesquiterpenoids is identified in the extractable portions of Bulgarian Neogene coals [10 - 12].

The relative content of the components determined in the pyrolysate flue gases (Table 1) is plotted in a „spider web diagram" (Fig. 4). Therein, the amounts of aliphatics (No.1, Table 1), aromatics (No.2 + No.6,

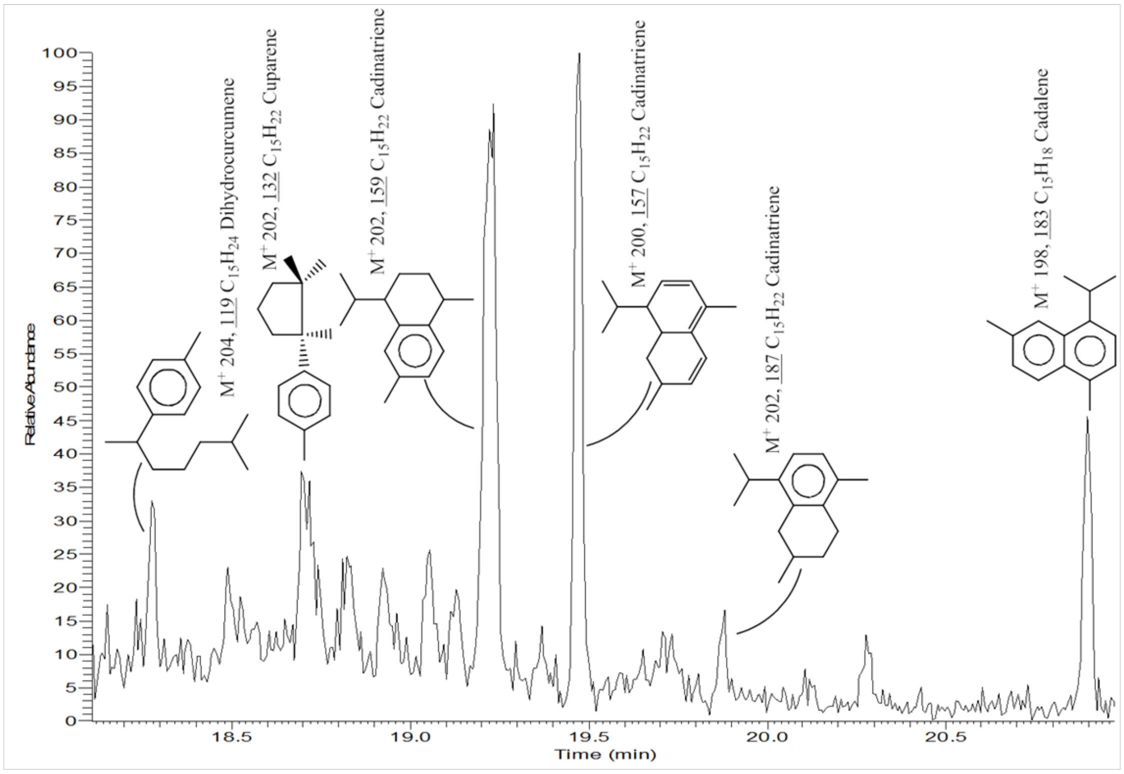

Fig. 3. Sesquiterpenoids in the first tube 250 - 550^{o}C pyrolysate of Stanianci lignite.

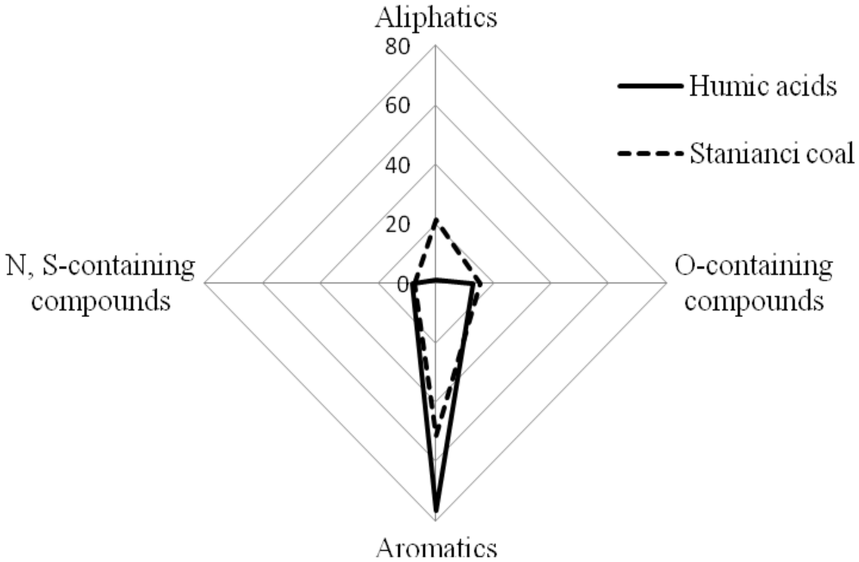

Fig. 4. “Spider web” diagram based on AP-TPR “off line” TD GC/MS data plotting relative content of clustered components representing group compositions of Stanianci lignite pyrolysate in comparison with Stanianci humic acids pyrolysate [6]. (solid line - Stanianci humic acid pyrolysate; dotted line - Stanianci lignite pyrolysate).

Table 1), O-containing (No.3 + No.4 + No.5, Table 1) and N- + S-containing (No.7 + No.8 + No.9, Table 1) compounds are correlated. Thus, about 96 % of the components observed are considered and identified. The clustered diagram presented visualizes some peculiarities mentioned above. The data referring to Stanianci lignite presented in Fig. 4 is compared with pyrolysate fractional composition of humic acids prepared from the same lignite [6]. Regardless of identical parent origin some differences in the pyrolysates emerge. Coal pyrolysate is characterized by essentially higher amounts of aliphatic structures and lower amounts of aromatic ones, higher amounts of methoxy phenols and lower amounts of S- + N- containing compounds when compared to the pyrolysate of humic acids prepared from the same coal.

CONCLUSIONS

AP-TPR coupled with TD-GC/MS detection system offers enhanced possibilities for coal analytical characterization. It allows the analysis of 40 mg sample on a molecular level with identification of a broad variety of components. Irrespective of the qualitative similarity of the pyrolysates of humic acids prepared from Stanianci lignite and the coal sample itself, the quantitative data interpretation outlines some structural peculiarities between them.

The results obtained can be used for the reconstruction of the coal depositional environment. Sesquiterpenoids, i.e. cuparene, as a specific chemosystematic marker for the presence of Cupressaceae/Taxodiaceae, argue for gymnospermous flora contribution to the coal-forming palaeomire.

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REFERENCES

1. S. C. Moldoveanu, Analytical pyrolysis of natural organic polymers, Elsevier Sci., 1998, 247.
2. J. Yperman, I. Maes, H. Van de Rul, S. Mullens, J. Van Aelst, D. Franco, Sulphur group analysis in solid materials by AP-TPR, Anal. Chim. Acta, 395, 1999, 143-155.
3. L. Gonsalvesh, Sulphur and organic sulphur alterations in biodesulphurized low rank coals, PhD thesis, BAS/Hasselt Univ., 2012, 214.
4. M. Stefanova, S. Marinov, J. Yperman, R. Carleer, Reductive pyrolysis of Miocene-aged lignite lithotypes using MS and GC/MS detection systems for analysis of organic sulphur groups, Fuel, 84, 2005, 71-79.
5. M. Stefanova, L. Gonsalvesh, S.P. Marinov, J. Czech, R. Carleer, J. Yperman, Reductive pyrolysis of leonardite humic acids, Bulg. Chem. Commun., 46, 2014, 123-128.
6. M. Stefanova, L. Gonsalvesh, S.P. Marinov, J. Czech, R. Carleer, J. Yperman, Reductive pyrolysis of Miocene-aged lignite humic acids (Bulgaria), Fuel, 165, 2016, 324-330.
7. S.S.J.Warne, Proximate analysis of coal, oil shale, low quality fossil fuels and related materials by thermogravity, Trends Anal. Chem.,10, 1991, 195-199.
8. L. Gonsalvesh, S.P. Marinov, M. Stefanova, Y. Yürüm, A.G. Dumanli, G. Dinler-Doganay,N. Kolankaya, M. Sam, R. Carleer, G. Reggers, E. Thijssen, J. Yperman, Biodesulphurized subbituminous coal by different fungi and bacteria studied by reductive pyrolysis. Part 1: Initial coal, Fuel, 87, 2008, 2533-2543.
9. B.R.T. Simoneit, Cyclic terpenoids of the geosphere, In: Johns R. B. (ed.) Biological markers in the Sedimentary Record, Amsterdam, Elsevier, 1986, 43–100.
10. M. Stefanova**,** D.R. Oros, A. Otto, B.R.T. Simoneit, Polar aromatic biomarkers in the Miocene Maritza-East lignite, Bulgaria, Org. Geochem., 33, 2002, 1079-1091.
11. M. Stefanova, K. Markova, S. Marinov, B.R.T. Simoneit, Biomarkers in the fossils from the Miocene-aged Chukurovo lignite, Bulgaria: sesqui- and diterpenoids, Bull. of Geosci. Czech Geol. Survey, 80, 2005, 93-97.
12. A. Bechtel, R. Sachsenhofer, A. Zdravkov, I. Kostova, R. Gratzer, Influence of floral assemblage, facies and diagenesis on petrography and organic geochemistry of the Eocene Bourgas coal and the Miocene Maritza-East lignite (Bulgaria), Org. Geochem., 2005, 36, 1498-1522.