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Features of pathological mechanisms of tooth damage in workers of chemical industries

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Abstract

INTRODUCTION. Under conditions of increasing exposure to chemical factors that predispose individuals to the development of pathology, the processes of hard-tooth-tissue destruction undergo modification not only in terms of their kinetics but also through the direct incorporation of exogenous chemical agents. These circumstances inevitably affect the macro- and microelement composition of enamel, as well as dentin and cementum in cases of disease progression. Obtaining reliable information on elemental composition is crucial for choosing appropriate treatment strategies and substantiating preventive measures.

AIM. To perform X-ray fluorescence analysis of teeth from employees of chemical enterprises, assessing qualitative and quantitative changes in elemental composition associated with pathological processes.

MATERIALS AND METHODS. The dental status of 100 workers and engineering personnel involved in the production of biologically active substances, paint-and-coating materials, and metal products, all of whom had direct contact with inorganic and organic reagents, was assessed. The control group included teeth from 50 individuals working at the same enterprises but not exposed to occupational hazards. The chemical composition of tooth hard-tissue samples was determined using an M4 TORNADO (Bruker) X-ray fluorescence spectrometer. The MultiPoint mode was used. The software provides the content of each element relative to the total amount of detected elements, considering the entire spectrum as 100%. A relatively constant Ca/P ratio served as an additional reference point for discussing deviations from normal values.

RESULTS. The identified diseases in the affected zones were accompanied by atypical accumulations of trace elements detected via XRF spectra. In several employees of a metallurgical plant, high titanium content – up to 1.14 wt% of total elemental content – was found in areas of dental erosion. Titanium levels in adjacent intact enamel were significantly reduced, although trace amounts were still present. In patients with long-term employment at a paint, coating, and anti-corrosion materials enterprise, potassium content in deep carious lesions reached 12.64%, and most individuals also showed substantial levels of zinc, barium, iron, sulfur, chlorine, manganese, and copper. Among workers of an agrobiological enterprise without hot workshops or industrial dust – due to multistage air purification and sterilization – caries prevailed. In employees of a chemical-pharmaceutical production facility, no cases of caries were detected; only non-inflammatory conditions such as increased tooth wear and wedge-shaped defects were diagnosed.

CONCLUSIONS. XRF analysis demonstrated that enamel demineralization processes in workers of chemical industries are accompanied by qualitative and quantitative changes in trace-element profiles within pathological zones. Environmental exposure results in the isomorphic and isoinic incorporation of elements into apatite structures of hard tooth tissues and disrupts the natural kinetics of mineralization and demineralization. The intensity of trace-element accumulation in tooth tissues is directly related to the degree of industrial air purification. Treatment and prevention of dental disorders in these workers must account for industry-specific occupational factors.

Keywords: chemical industries, harmful occupational factors, X-ray fluorescence analysis, Ca/P ratio, occupational dental erosion, tooth mineral structure

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Особенности механизмов патологии зубов у сотрудников химических предприятий

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Резюме

ВВЕДЕНИЕ. В условиях усиления влияния химического фактора, предрасполагающего к возникновению патологии, происходит модификация процессов деструкции твердых тканей зубов и в плане изменения их кинетики, и прямого включения в них экзогенных химических агентов. Эти обстоятельства не могут не влиять на макро- и микроэлементный состав не только эмали, но и дентина, и цемента в случае усугубления заболевания. Получение достоверной информации по составу элементов имеет существенное значение для выбора правильной тактики лечения и обоснования профилактических мер.

ЦЕЛЬ. Провести рентгенофлуоресцентный анализ твердых тканей зубов сотрудников химических предприятий, с оценкой качественных и количественных изменений элементного состава, сопровождающих развитие патологии.

МАТЕРИАЛЫ И МЕТОДЫ. Был определен стоматологический статус 100 рабочих и инженерно-технических работников, занятых в производстве биологически активных веществ, лакокрасочных материалов, металлопродукции, имевших непосредственный контакт с неорганическими и органическими реагентами. Контрольную группу составили зубы 50 человек, работавших на этих предприятиях в условиях отсутствия профессиональных вредностей. Химический состав образцов твердых тканей зуба определяли на рентгенофлуоресцентном спектрометре M4 TORNADO (Bruker). В ходе работы использовали режим MultiPoint. Программа показывает содержание данного элемента относительно суммы всех определяемых элементов, принимая весь полученный спектр за 100%. Ориентиром для обсуждения наблюдаемых отклонений содержания элементов от нормы служила, в том числе, относительно постоянная величина индекса Ca/P.

РЕЗУЛЬТАТЫ. Обнаруженные заболевания в зонах поражения зубов сопровождаются нетипичными накоплениями микроэлементов, которые зарегистрированы спектрами РФА. У ряда сотрудников металлургического завода, в области эрозии зубов отмечено высокое содержание титана, до 1,14 % по массе от общего содержания элементов. В составе интактной эмали, расположенной рядом с эрозией, содержание титана резко снижено, но все же он присутствует. У пациентов, длительное время проработавших на предприятии, производящем лакокрасочные и антикоррозионные материалы, содержание калия в зоне глубокого кариеса составило до 12,64 %, а также у большинства пациентов показано довольно существенное присутствие цинка, бария, железа, серы, хлора, марганца, меди. У обследованных работников агробиологического предприятия, на котором отсутствуют горячие цеха и в явном виде промышленная пыль, поскольку воздух в промзоне подвергается многоступенчатой очистке и стерилизации, в большей степени преобладает кариес. Среди обследованного персонала химико-фармацевтического производства практически не выявлено случаев кариеса, диагностированы заболевания невоспалительного характера, в основном повышенная стираемость и клиновидные дефекты зубов.

ВЫВОДЫ. Методом РФА установлено, что у сотрудников химических производств процессы деминерализации эмали зубов сопровождаются качественным и количественным изменением номенклатуры микроэлементов в зоне патологии. Воздействие элементов из окружающей среды состоит в их изоморфном и изоинном внедрении в апатитные структуры зубов и нарушении естественной кинетики процессов минерализации и деминерализации. Интенсивность накопления микроэлементов в твердых тканях зубов непосредственно связана со степенью очистки промышленного воздуха. Терапия и профилактика стоматологических проблем должна учитывать специфику производственной деятельности работников предприятий.

Ключевые слова: химические предприятия, вредный фактор, рентгенофлуоресцентный анализ, индекс Ca/P, профессиональная эрозия зубов, минеральная структура зуба

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INTRODUCTION

In numerous publications of recent years, the chemical, biochemical, and physical aspects of various dental diseases have been comprehensively addressed under both *in vitro* and *in vivo* conditions. These studies describe fundamentally different mechanisms of hard dental tissue destruction occurring as a result of microbial activity (dental caries) as well as widely prevalent non-carious dental disorders that are non-inflammatory in nature, primarily including dental erosion, wedge-shaped defects, and increased tooth wear [1–5].

An increased research focus has been placed on the clinical manifestations of dental diseases among workers exposed to hazardous occupational conditions, particularly those employed in chemical industries [6; 7], as they are subject to a significantly higher risk. It is evident that under conditions of enhanced chemical exposure predisposing to the development of pathology, the processes of hard dental tissue destruction are modified not only in terms of their kinetics but also through the direct involvement of exogenous chemical agents. These factors inevitably affect the macro- and microelemental composition not only of enamel but also of dentin and cementum in cases of disease progression.

Obtaining reliable information on elemental composition is of critical importance for the selection of appropriate therapeutic strategies and for substantiating preventive measures aimed at reducing the risk of dental damage among personnel involved in chemical raw material processing, organic or inorganic synthesis, or related analytical activities.

As has been repeatedly demonstrated [2; 4], the acquisition of accurate and statistically significant data on elemental content in hard dental tissues is optimally achieved using modern X-ray fluorescence spectrometers designed for direct analysis of solid surfaces. One of the key advantages of X-ray fluorescence analysis (XRF) is that the analyzed samples do not require complex sample preparation.

AIM

To perform X-ray fluorescence analysis of the hard dental tissues of employees of chemical enterprises, with an assessment of qualitative and quantitative changes in elemental composition accompanying the development of pathology.

MATERIALS AND METHODS

The study was conducted at the Departments of Therapeutic Dentistry and Endodontics, as well as General and Bioorganic Chemistry of the Russian University of Medicine (Ministry of Health of the Russian Federation), and in the laboratories of the N.S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.

The dental status of 100 workers and engineering-technical personnel involved in the production of biologically active substances, paints and coatings, and metal products, who had direct contact with inorganic and organic reagents, was assessed. The control group consisted of teeth obtained from 50 individuals em-

ployed at the same enterprises under conditions without occupational hazards.

Teeth subjected to X-ray fluorescence analysis were, in all cases, extracted for periodontal or orthodontic indications. Only intact teeth without signs of prior dental treatment were used. The samples were cleaned of soft tissues, disinfected, and stored in distilled water at 4°C.

The chemical composition of hard dental tissue samples was determined using an M4 TORNADO X-ray fluorescence spectrometer (Bruker), a micro-XRF analyzer designed for non-destructive qualitative and quantitative material analysis. The method is based on the interaction of elements present in the sample with high-energy X-ray radiation, resulting in the emission of detectable secondary X-ray radiation (X-ray fluorescence) characteristic of each atomic species. The operating unit of the instrument is a rhodium fine-focus X-ray tube (maximum excitation voltage 50 kV, power 30 W, current 600 µA). Measurements were performed in the Multi-Point mode, allowing analysis at several points within a selected area of the enamel surface.

During the analysis, the X-ray beam was directed at a predetermined point on the sample surface, and elemental composition was determined for a spot with a diameter of 20 µm. The computer integrated into the instrument processed the data using specialized software and provided measurement results for the selected point as an average value over 100 pulses, presented as a spectrum of detected elements. The resulting spectrum was subsequently converted into a table of mass percentage ratios of the constituent elements in the analyzed area. The software reports the content of each element relative to the total sum of all detected elements, considering the entire spectrum as 100%. As is well known, X-ray fluorescence analysis does not allow sufficiently accurate determination of elements from the first two periods of the Periodic Table or sodium; however, this limitation did not impede the achievement of the study objectives.

The instrument was calibrated using a standard sample of calcium dihydrogen phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, with respect to calcium and phosphorus content. The measurement accuracy was 0.01%. Statistical analysis of the obtained data was performed using a personal computer and the software package *Statistica 9.0*.

In discussing deviations of elemental content from normal values, reference was made, among other parameters, to the relatively constant Ca/P ratio. According to the literature, this ratio for enamel resistant to acid exposure ranges from 1.6 to 2.1 by mass. In the present study, the Ca/P ratio for enamel samples of healthy teeth from the control group ranged from 1.9 to 2.2.

RESULTS

The detected diseases in the affected areas were accompanied by atypical accumulations of trace elements, as evidenced by X-ray fluorescence (XRF) spectra. Without addressing the pathways by which these elements enter the hard dental tissues (potentially via industrial air), which constitutes the subject of a separate investigation, it can be stated that an association was observed

between elevated concentrations of specific elements or groups of elements and the type of dental pathology.

For example, in a number of employees of a metallurgical plant that utilizes zinc-, aluminum-, and other non-ferrous metal-containing alloys in its core operations, a high titanium content was detected in areas of dental erosion, reaching up to 1.14 wt% of the total elemental content registered in the spectrum. These observations were made in patients whose oral cavities contained no metallic restorations or prosthetic structures. As an illustration, Fig. 1 presents a fragment of one such tooth (Patient No. 1), together with the corresponding X-ray

fluorescence spectrum and the numerical values of the relative elemental contents at the analyzed points.

Similarly elevated titanium concentrations were identified in erosion zones of teeth in a number of other patients from this enterprise. In Patient No. 2, multiple cervical non-carious lesions were diagnosed, including concurrent erosions and wedge-shaped defects, with a titanium mass fraction of 1.06%.

Of particular interest is the observation that in the intact enamel adjacent to the erosion (Patient No. 1), the titanium content was markedly reduced, yet still detectable, as evidenced by the data presented in Fig. 2.

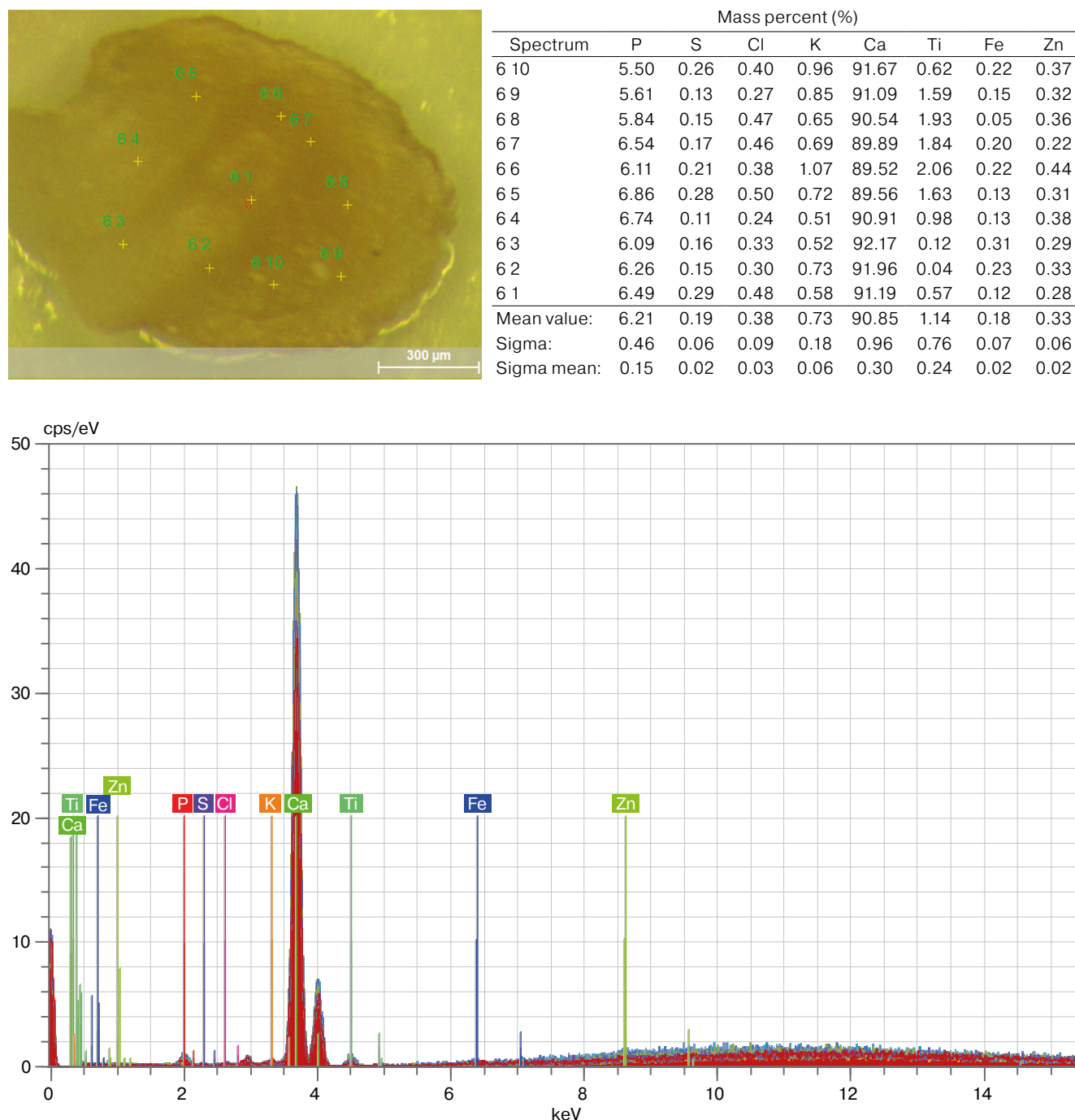
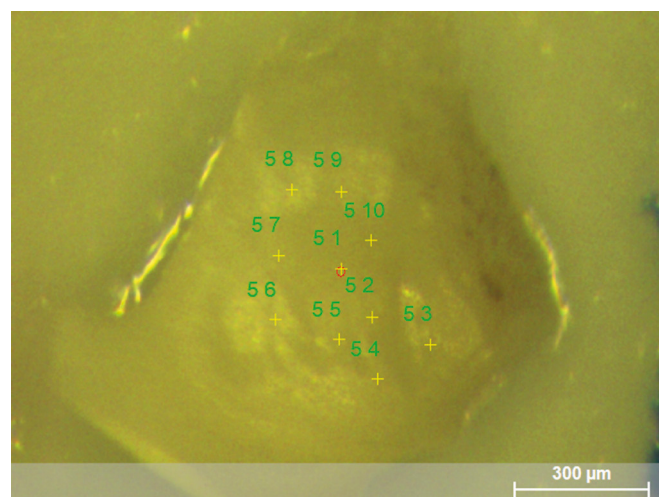


Fig. 1. Data on the analysis of the tooth erosion site of patient No. 1 (XRF, MultiPoint mode)

Рис. 1. Данные по анализу участка эрозии зуба пациентки № 1, (РФА, режим MultiPoint)

Notably, a high potassium content, reaching up to 1.86% in the affected areas, was observed; in some cases, though not consistently, this was associated with elevated titanium levels. Data reported by researchers from different laboratories regarding potassium content in healthy enamel are contradictory, although potassium is consistently regarded as a trace element. Our previous results obtained using laser mass spectrometry [8] demonstrated that the potassium mass fraction in intact enamel does not exceed 0.1% and is usually considerably lower.

In Patient No. 3, who had been employed for an extended period at an enterprise producing paints, coatings, and anticorrosive materials, the potassium content in the area of deep caries reached 12.64%, as shown in Fig. 3. In the same region, a substantial presence of zinc, barium, iron, sulfur, chlorine, manganese, and copper was also detected. Manganese accompanied by a similar spectrum of associated trace elements was identified in another employee of the same enterprise, who presented not with caries but with dental erosion.



Spectrum	Mass percent (%)				
	P	Ca	Ti	Zn	Sr
5 10	8.30	90.86	0.26	0.13	0.46
5 9	7.73	91.73	0.16	0.13	0.25
5 8	8.19	91.14	0.26	0.10	0.31
5 7	7.81	91.42	0.31	0.14	0.32
5 6	8.08	91.44	0.06	0.10	0.31
5 5	8.39	90.91	0.25	0.10	0.35
5 4	8.36	90.94	0.20	0.11	0.39
5 3	8.30	90.67	0.52	0.13	0.38
5 2	8.79	90.45	0.30	0.15	0.32
5 1	8.03	91.29	0.27	0.12	0.29
Mean value:	8.20	91.09	0.26	0.12	0.34
Sigma:	0.31	0.39	0.12	0.02	0.06
Sigma mean:	0.10	0.12	0.04	0.01	0.02

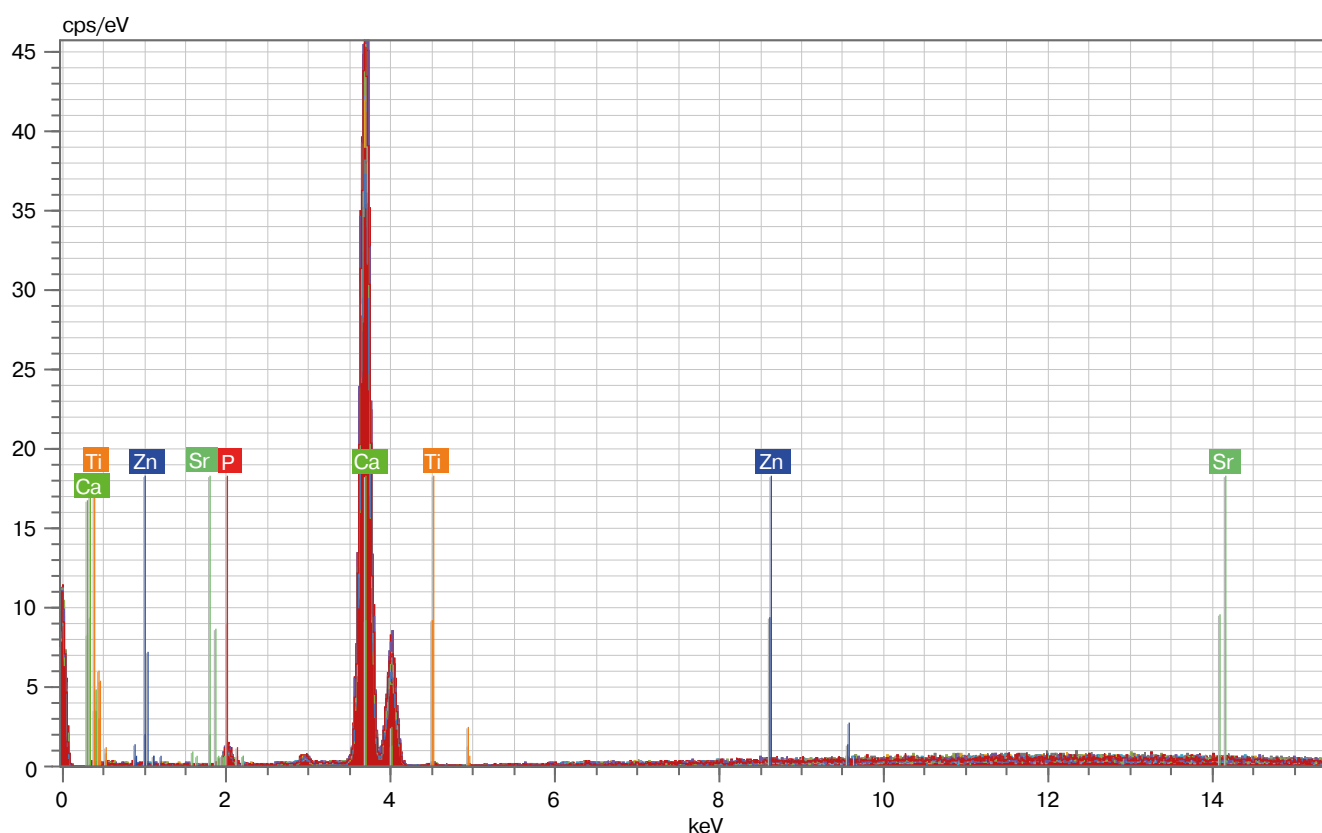
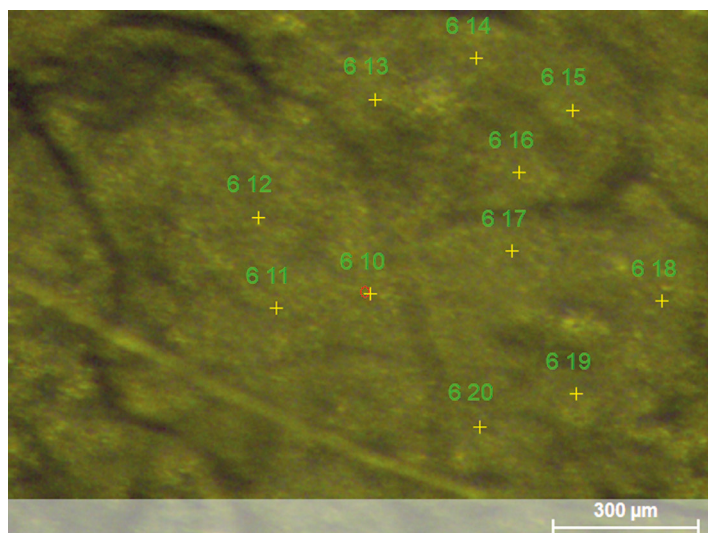


Fig. 2. Data on the analysis of an intact enamel area near the erosion of tooth in patient No. 1, (XRF, MultiPoint mode)

Рис. 2. Данные по анализу участка интактной эмали рядом с эрозией зуба пациентки № 1, (РФА, режим MultiPoint)



Mass percent (%)												
Spectrum	P	S	Cl	K	Ca	Ti	Mn	Fe	Cu	Zn	Sr	Ba
6 20	4.07	1.36	1.89	11.86	75.61	0.01	0.25	0.85	0.43	2.22	0.56	0.88
6 19	3.91	1.16	1.93	12.06	76.61	0.00	0.25	0.77	0.45	1.68	0.37	0.80
6 18	3.99	1.42	1.95	9.96	78.92	0.00	0.25	0.74	0.39	1.55	0.37	0.45
6 17	4.21	1.57	2.19	11.52	74.23	0.00	0.23	0.72	0.35	1.75	0.75	2.49
6 16	4.57	1.57	2.18	12.55	74.50	0.00	0.31	0.71	0.50	1.70	0.53	0.88
6 15	5.05	1.73	2.65	14.27	71.71	0.00	0.33	0.93	0.47	1.75	0.44	0.67
6 14	5.69	1.97	3.80	18.52	65.10	0.00	0.36	1.03	0.57	2.19	0.49	0.28
6 13	4.97	1.77	2.52	12.61	73.61	0.00	0.34	0.82	0.48	2.09	0.49	0.28
6 12	4.46	1.53	2.12	13.58	74.33	0.00	0.21	0.75	0.41	1.85	0.43	0.33
6 11	4.43	1.41	2.02	11.28	76.78	0.00	0.28	0.83	0.43	1.87	0.37	0.30
6 10	4.40	1.24	1.81	10.83	77.82	0.00	0.26	0.70	0.41	1.73	0.28	0.54
Mean value:	4.52	1.52	2.28	12.64	74.47	0.00	0.28	0.80	0.44	1.85	0.46	0.72
Sigma:	0.53	0.24	0.57	2.29	3.72	0.00	0.05	0.10	0.06	0.22	0.12	0.63
Sigma mean:	0.16	0.07	0.17	0.69	1.12	0.00	0.01	0.03	0.02	0.07	0.04	0.19

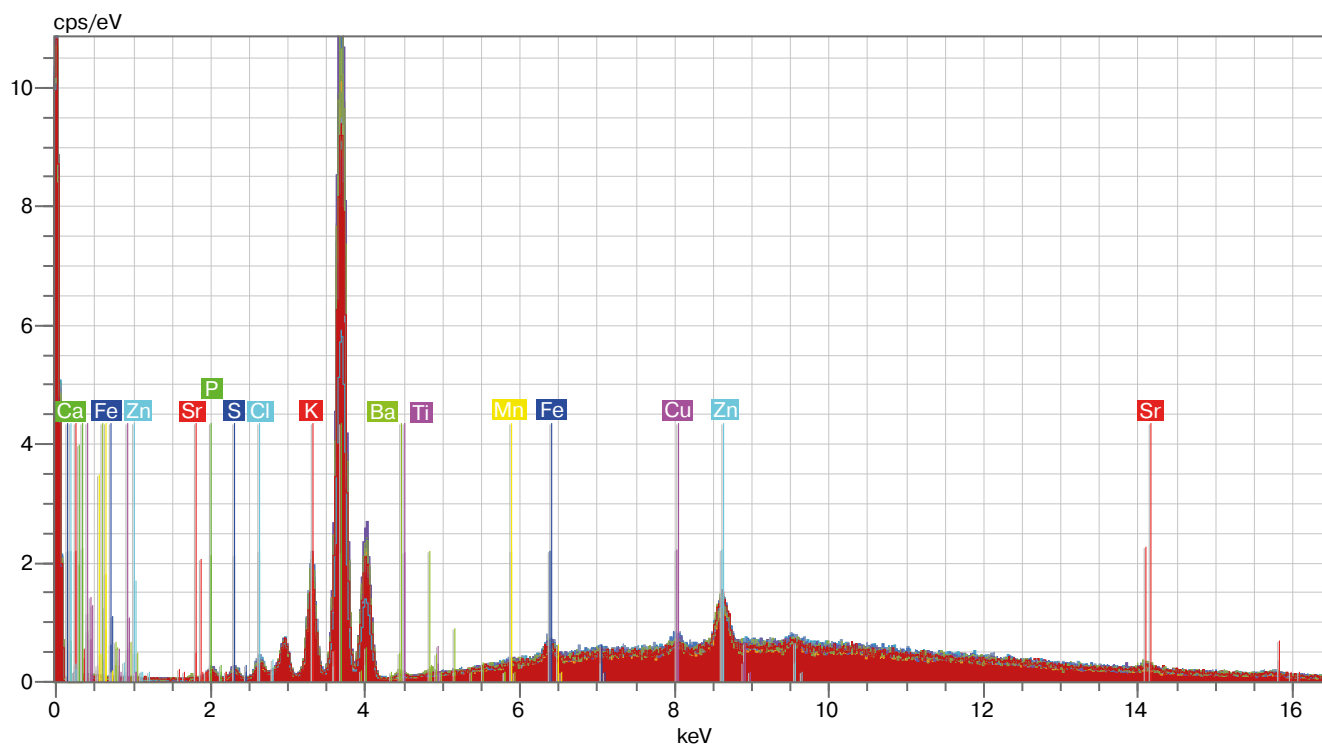
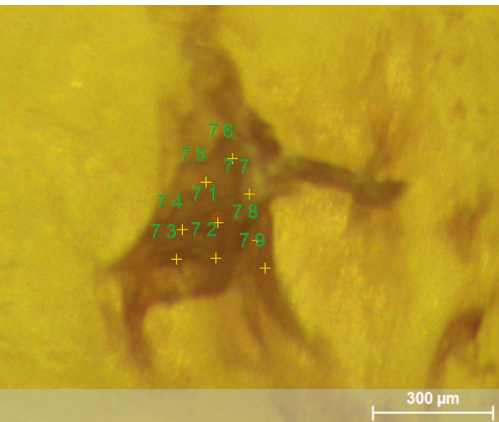


Fig. 3. Data on the analysis of the deep caries area of tooth No. 3, (XRF, MultiPoint mode)

Рис. 3. Данные по анализу участка глубокого кариеса зуба пациента № 3, (РФА, режим MultiPoint)

The nature of predominant negative changes in the oral cavity among the patient sample appears to be, to some extent, specific to each enterprise engaged in chemical production. Among the workers examined at an agrobiological facility – where there are no hot workshops and industrial dust is not present due to multi-stage air purification and sterilization in the production area – dental caries was the most prevalent condition. For example, Patient No. 4 exhibited pronounced light-brown pigmentation, with the corresponding spectral data presented in Fig. 4. The production processes at this enterprise involve various biological objects, nutrient media, and pharmacologically active compounds, which may explain the presence of a wide range of elements in the inflammatory focus, including chlorine, zinc, strontium, potassium, titanium, barium, iron, and sulfur.



Spectrum	Mass percent (%)									
	P	S	Cl	K	Ca	Ti	Fe	Zn	Sr	Ba
79	3.13	0.90	0.84	1.75	91.99	0.01	0.48	0.51	0.19	0.20
78	3.20	0.73	0.80	1.70	92.12	0.10	0.51	0.49	0.15	0.20
77	3.75	0.65	0.68	1.51	91.95	0.17	0.44	0.43	0.16	0.27
76	3.64	0.47	0.59	1.38	92.76	0.15	0.35	0.42	0.13	0.11
75	3.47	0.59	0.65	1.35	92.71	0.15	0.26	0.49	0.14	0.17
74	1.31	1.01	1.10	2.23	92.36	0.11	0.50	0.74	0.29	0.36
73	1.06	1.37	1.46	2.82	90.59	0.31	0.79	0.78	0.28	0.53
72	1.36	1.28	1.57	2.91	89.57	0.98	0.81	0.80	0.27	0.46
71	1.74	1.28	1.42	2.74	89.33	0.90	0.65	0.76	0.33	0.85
Mean value:	2.52	0.92	1.01	2.04	91.49	0.32	0.53	0.60	0.21	0.35
Sigma:	1.12	0.33	0.38	0.64	1.32	0.36	0.19	0.16	0.08	0.23
Sigma mean:	0.37	0.11	0.13	0.21	0.44	0.12	0.06	0.05	0.03	0.08

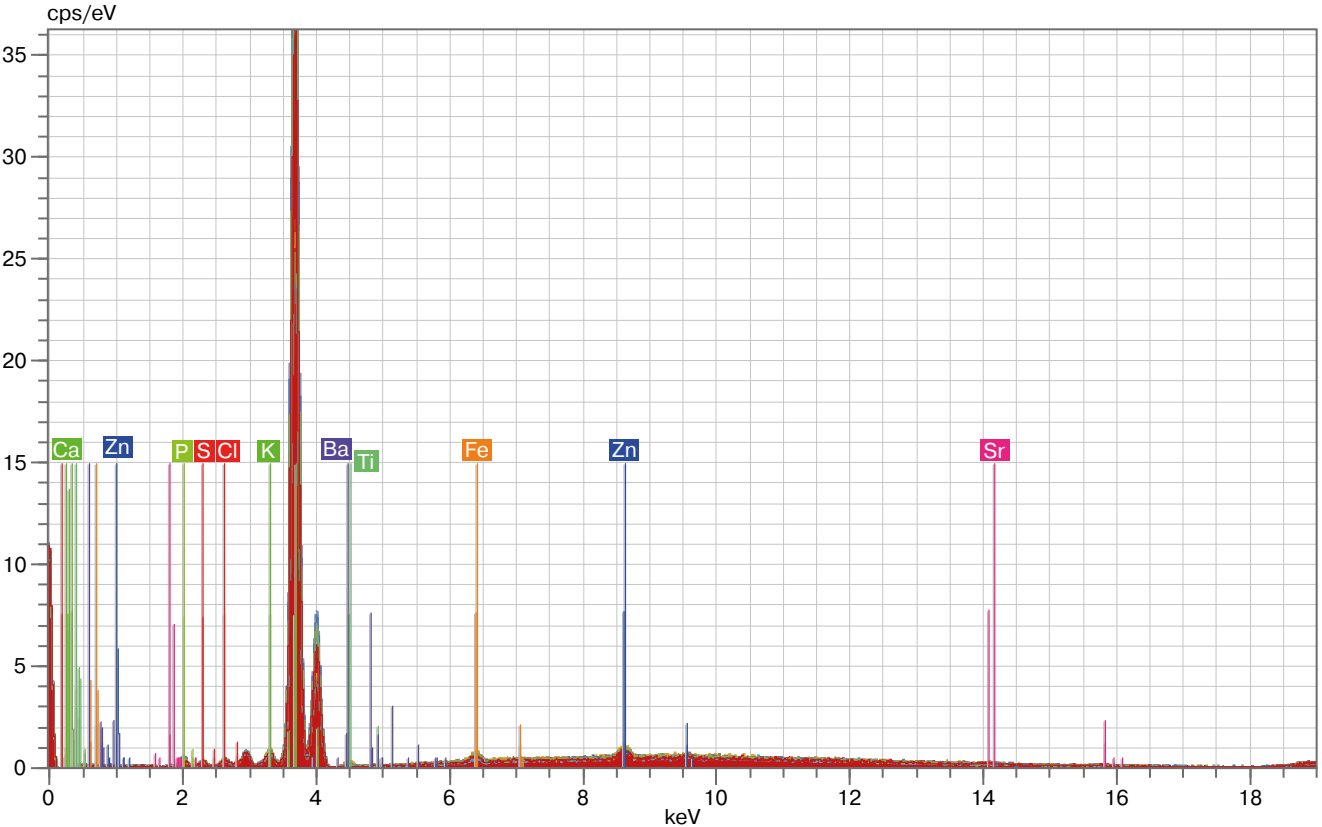
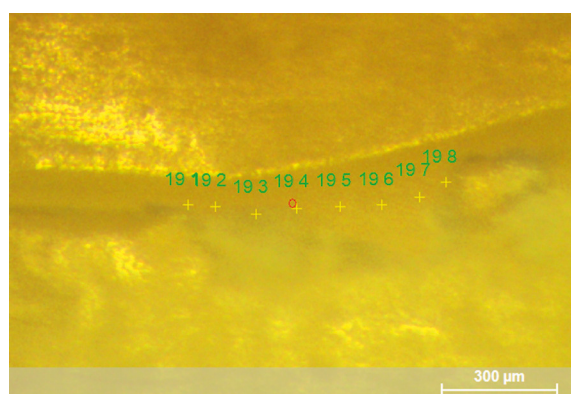


Fig. 4. Data on the analysis of the caries site of the pigmented tooth of patient No. 4, (XRF, MultiPoint mode)
Рис. 4. Данные по анализу участка кариеса пигментированного зуба пациента № 4, (РФА, режим MultiPoint)



Spectrum	Mass percent (%)				
	P	Ca	Fe	Ni	Zn
19 8	7.44	91.85	0.13	0.18	0.39
19 7	7.06	92.47	0.09	0.12	0.27
19 6	8.01	91.72	0.04	0.08	0.15
19 5	9.15	90.45	0.08	0.11	0.21
19 4	7.91	91.61	0.07	0.11	0.31
19 3	7.83	91.65	0.10	0.10	0.33
19 2	9.00	90.52	0.12	0.09	0.27
19 1	7.99	91.54	0.12	0.06	0.29
Mean value:	8.05	91.48	0.09	0.10	0.28
Sigma:	0.71	0.68	0.03	0.03	0.07
Sigma mean:	0.25	0.24	0.01	0.01	0.03

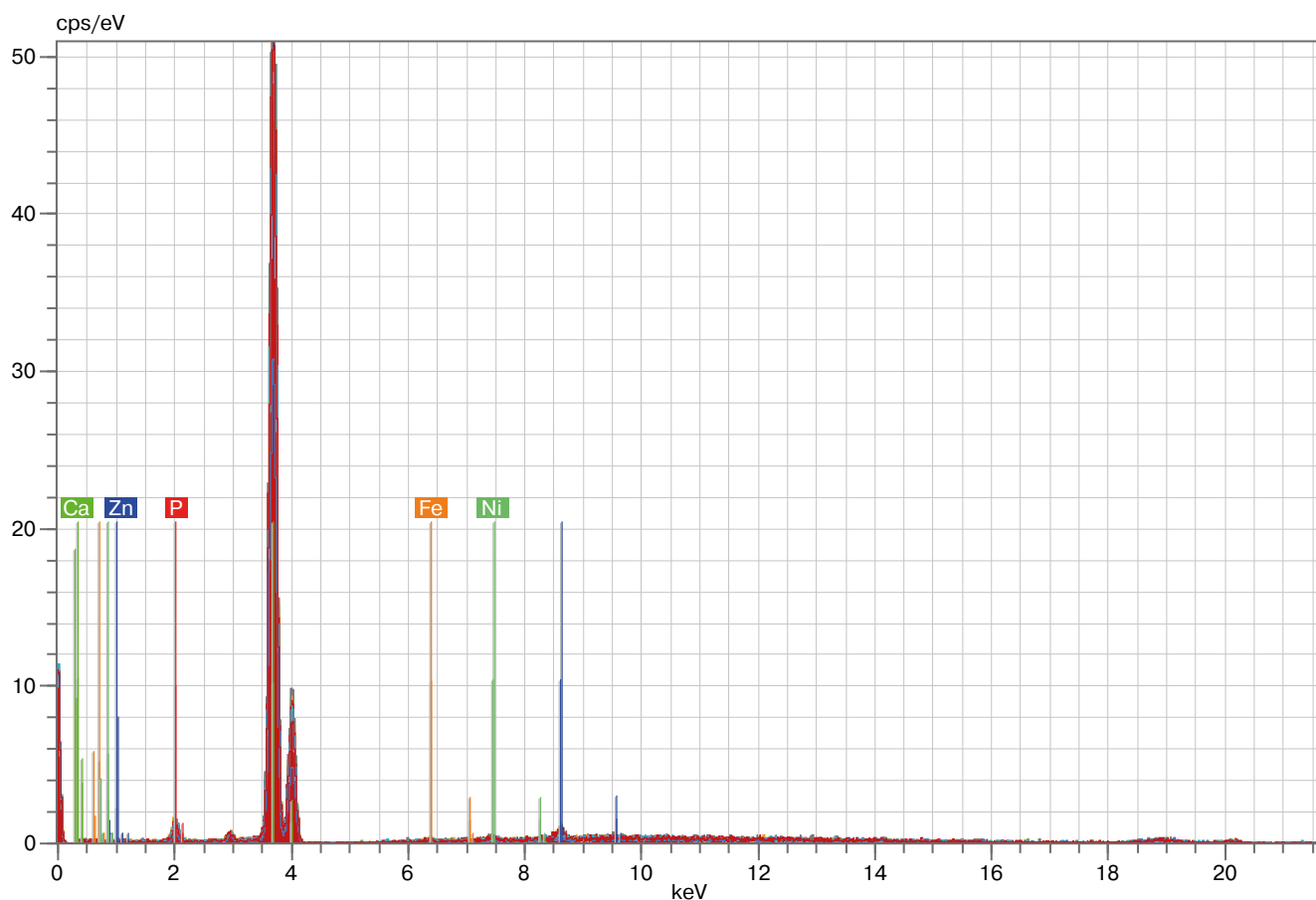


Fig. 5. Data on the analysis of the wedge-shaped tooth defect in patient No. 5 (XRF, MultiPoint mode)

Рис. 5. Данные по анализу участка клиновидного дефекта зуба пациента № 5, (РФА, режим MultiPoint)

DISCUSSION

The findings obtained in this study logically integrate into the broader body of knowledge generated by numerous investigations aimed at identifying the characteristics of dental disease progression in workers involved in chemical production [9–12]. Harmful occupational factors shift the dental status of individuals toward pathology, with exogenous intoxication clearly affecting the macro- and microelement composition not only in the lesion area but also in adjacent regions where clinical signs of disease are absent, yet the elemental composition of the tooth surface already differs from normal both qualitatively and quantitatively.

The elevated titanium content observed in erosion zones of teeth among several employees of a metallurgical enterprise is of particular concern for occupational health services, which would likely identify the source of this trace element exposure. Titanium itself is known to be one of the most biocompatible metals, widely used in medicine, including orthopedic and dental implants. However, first, the examined patients had no metallic restorations in the oral cavity, and second, titanium in the hard dental tissues was present in oxidized forms rather than as the pure metal. Whereas titanium was once considered biologically inert, recent studies increasingly highlight its potential toxicity: tita-

nium particles and ions can accumulate in tissues and induce inflammatory responses [13].

Regarding the concurrent elevation of potassium and titanium in the pathological zones, such an association requires further investigation, as these elements perform distinct biological functions and are not directly linked in biochemical pathways. It should be noted that among employees of the metallurgical plant, non-carious lesions predominated, and the Ca/P ratio, exceeding the normal range and reaching 3.27, indicates a canonical pattern of enamel demineralization characterized by more rapid dephosphorylation relative to decalcification. Notably, XRF spectra from intact enamel adjacent to erosion returned the Ca/P ratio to 2.19, effectively restoring it too normal.

In workers at the enterprise producing paints and anticorrosive materials, the elemental composition within carious lesions – including essential elements – exhibited considerable diversity and significant quantitative deviations from normal, particularly for iron, sulfur, chlorine, zinc, and barium. The presence of these elements, incorporated as cations and anions into the lesion, suggests their direct or indirect involvement in mineralization processes, whereby their isomorphic or isoelectronic integration into apatite-like structures alters the usual kinetics of the opposing demineralization process. While classical caries progression typically reduces the Ca/P ratio from the normal range of 1.9–2.1 [14], in this patient group it increased up to 3.24, indicating intensified dephosphorylation relative to decalcification. This effect may be linked to the simultaneous presence in the lesion and saliva of salts comprising cations of strong bases (strontium, potassium, barium) and anions of weak acids (sulfides, sulfites), whose hydrolysis produces an alkaline environment that reduces the concentration of hydronium ions responsible for calcium substitution in hydroxyapatite [15–17].

At the agrobiological enterprise, the number of caries cases among examined workers was more than twice that of recorded increased tooth wear, potentially reflecting variations in work across different production areas. XRF spectra from carious lesions demonstrated not only a wide range of trace elements, as in previous examples, but also similar deviations of the Ca/P ratio above normal, reaching 5.92 in one patient. In contrast,

spectra from intact enamel adjacent to the lesion reduced this ratio to 2.98.

For the subset of patients at the same enterprise exhibiting increased tooth wear, XRF spectra revealed no deviations from normal. The Ca/P ratio ranged from 2.07 to 2.46, a slight elevation consistent with observations for non-inflammatory hard tissue lesions [18].

Among employees of the chemical-pharmaceutical enterprise, all deviations from normal dental status were non-inflammatory. Erosive lesions and wedge-shaped defects occurred with roughly equal frequency. Detected trace elements showed only sporadic and minor quantitative deviations and were typical in type. In nearly all cases, the macroelement Ca/P ratio was slightly elevated, reflecting standard enamel demineralization processes in the absence of microbial involvement.

CONCLUSION

1. X-ray fluorescence analysis (XRF) demonstrated that, in employees of chemical production facilities, enamel demineralization is accompanied by both qualitative and quantitative changes in the microelement composition within pathological zones. In nearly all cases, the Ca/P ratio was increased, in some instances reaching 3.27, indicating a canonical pattern of enamel demineralization characterized by more rapid dephosphorylation relative to decalcification.

2. Environmental elements exert their effect through isomorphic and isoelectronic incorporation into the apatite structures of hard dental tissues, disrupting the natural kinetics of mineralization and demineralization. The detection of iron, sulfur, chlorine, zinc, and barium, incorporated as cations and anions into inflammatory foci, indicates their direct or indirect involvement in the mineralization process.

3. The intensity of microelement accumulation in hard dental tissues is directly related to the degree of industrial air purification from toxic chemical agents. For example, in erosion zones of teeth from metallurgical plant employees, titanium content reached as high as 1.14%.

4. Therapy and preventive strategies for dental disorders should take into account the specific occupational exposures of employees working in chemical production facilities.

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